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EXAMINER

PIERCE, WILLIAM M

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Please find below and/or attached an Office communication concerning this application or proceeding.

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**BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES**

Application Number: 09/832,141
Filing Date: April 09, 2001
Appellant(s): CHRISMAN, JOHN W.

**MAILED
SEP 12 2007
GROUP 3700**

Brick Power
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed 5/15/07 appealing from the Office action mailed 6/30/06.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

(2) Related Appeals and Interferences

The case as been previously appealed on 4/17/03 with a subsequent Examiner's Answer. Appellant filed on RCE 6/28/05 prior to any Decision by the Board. The examiner is not aware of any other related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

4,722,815	Shibanai	2-1988
4,762,493	Anderson	8-1998

4,293,602

Coffey et al.

10-1961

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 1-3, 5, 7, 8, 10-27, 29 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over what is old and well known in bowling balls in view of Shibantai and Coffey.

As to claims 1-3, 5, 7, 10-19, 20-27, 29 and 31, bowling balls of nonporous polymeric two-part thermosetting resin is old and well known. This is admitted old at the bottom of pg. 2 of Appellant's specification. Lacking in bowling balls is the use of a fragrance. However, perfumed additives and perfumed polymers intended for the purpose of making plastic articles with a fragrance are also well known. Shibantai teaches compounds to be included in synthetic resin products in order to enhance their smell. He clearly teaches the use of epoxy (col. 7, ln. 56) which is known in the art to be available as a one-part or two-part resin. While there is no direct teaching of using his compound in a bowling ball, it has been held that, in evaluating a reference, it is proper to take into account not only the specific teaching of the reference(s) but also the inferences which one skilled in the art would reasonably be expected to draw therefrom. In re Preda, 401 F.2d 825, 826, 159 USPQ 342,344 (CCPA 1968). Additionally, one must observe that an artisan must be presumed to know something about the art apart from what the references disclose (see In re Jacoby, 309 F.2d, 513,516, 135 USPQ 317, 319 (CCPA 1962). In line with this, one skilled in the art would clearly have found it obvious to have applied perfumed compounds, such as Shibantai's in order to make a bowling ball smell better. Where the claims call for a two-part resin and the fragrance being dissolved therein, Shibantai directly teaches (col. 7, ln. 56) that smell can be added to "epoxy resin coatings". Epoxy resin is a known "two part" resin. See evidence in the copy of Handbook of Reinforced Plastics, "Epoxy Resins", pg. 71, col. 1, ln. 20, appended to this Answer, where it shows that "cure may be established using materials classed as hardeners or curing agents". Shibantai also teaches that "it is also possible to mix perfume...with a synthetic resin compound followed by molding" (col. 1, ln. 26) but that this "direct addition of perfume...to synthetic resin compound

is not as effective as it seems" (col. 1, 35). Hence Shibantai goes on to teach an improved more effective method of adding fragrance to a product that includes forming an inclusion compound consisting of perfume included in cyclodextrin. While Shibantai does not detail the old and known methods of "mixing perfume" and "direct addition of perfume" that is at least partially dissolved within the resin, such are considered old when one further considers Coffey et al. as an example. Coffey teaches that it is an old expedient and would have been obvious to mix fragrances to two part resins in the forming of a fragrances polymer product. Edwards and Wilbert, are further examples of direct mixing of fragrances with a polyurethane prior to molding. The art is replete with the successful addition of fragrance to two part polymer products. The motivation is simply to "impart to other polymeric products pleasant odors" (Wilbert, col. 1, ln. 57). The amount of fragrance as called for in claim 8 is considered an obvious matter of choice depending upon how strong of a smell is desired. The examiner's position is in line and fully supported by the findings of the Courts in the recent decision to *KSR Int'l Co. v. Teleflex, Inc.*, No 04-1350 (U.S. APR. 30, 2007).

Claims 9, 32 and 33 are rejected under 35 U.S.C. 103(a) as being unpatentable over bowling balls in view of Shibantai and further in view of Anderson.

Applying a pigment to polymer resin products to give them color is old and well known. Anderson teaches that it is old to apply a color that correlates to a fragrance in a product. To have done so with a bowling ball would have been obvious to one skilled in the art for the novelty.

(10) Response to Argument

(B) Rejection under 103

(1) and (2)

Appellant remarks pertaining to the "applicable law" and his interpretation of the references on pgs. 6-8 with no further response deemed necessary.

(3)

Appellant's assessment of a "two-part resin" is not complete and in line with what is disclosed in his specification. Appellant is not entitled at this point to change the meaning by stating that two-part is intended to mean what is known in the polymer art in attempts to evade the applied art. *ACTV, Inc. v. The Walt Disney Company*, 346 F.3d 1082, 1092, 68 USPQ2d 1516, 1524 (Fed. Cir. 2003) sets forth that where there was no expressed definition given for the term in the specification, the term should be given its broadest reasonable interpretation consistent with the intrinsic record and take on the ordinary and customary meaning attributed to it by those of ordinary skill in the art. The question here is are those of ordinary skill in the art bowlers or polymer scientists? Here the broadest reasonable interpretation of "two-part" is considered customary to one skilled in the art of bowling. Most broadly "two-part" would be given its ordinary meaning of a resin having two parts, a first part and a second part. This interpretation is commensurate with what appellant meant by two-part in his discussing of his invention in his specification where it conveys most broadly that any plastic made up of two components can be considered a "two-part resin". Specifically, the specification notes that "conventionally, bowling balls have been formed from machineable, thermosetting plastic materials." (pg. 2, [0002]) and at paragraph [0004] of pg. 2 discusses reactive polymers that require the presence of a catalyst for polymerization requiring only an A-side and a B-side (i.e. two parts). Nowhere in the specification does appellant consider or define polymers requiring a catalyst (such as the ones discussed in paragraph [0004]) to be defined as "two-part resins" that require "mixing" as alluded to in his Brief. From appellant's specification, he has defined a two-part resin to be broader than what is commonly referred to in the industry. From his specification, a "two-part resin is most broadly one having an "two parts", an A-side and a B-side. His definition of a "two-part resin" used for his invention fits what is commonly referred to in the plastics industry as a "one-part resin" because these resins are known to require a second part or curing agent in addition to their base component. (See pg. 2, col. 1, ln. 8, of Three Bond Technical News, One-Part Epoxy Resin at <http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech19.pdf> appended to this Answer). Since appellant's specification never compares and contrasts the differences between one and two part resin or specifically discloses that his invention is only drawn to a two-part resin that is conventionally used, his

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later use of the term-two-part resin is any resin most broadly having two parts and A-side and a B-side, which encompasses both "one-part" and "two-part" resins known in the plastics art since they are known to use the same epoxy resins and a curing agent. Both require mixing and blending of the two components. The difference is that one-part resin can be considered to be a "premixed" compound and two-part resin must be mixed just before manufacture. (See <http://www.adhesivestoolkit.com/Docu-Data/AdhesiveTypesOverview.xtp> that states;

"Two-part epoxy adhesives start to react under ambient conditions once the two components have been mixed together and are often termed room-temperature (RT) curing adhesives because of this. The reaction mechanism is still affected by temperature and as a rule of thumb the reaction rate approximately doubles for every 10°C rise in temperature i.e. an epoxy which takes 1 hour to cure at 20°C, will cure in 15 minutes at 40°C. Conversely the cure time will double as the temperature drops by 10°C. Complete cure times at ambient temperatures for two-part systems range from ~10mins to several days.

Single-part epoxy adhesives are available in liquid, paste or film form. These adhesives require heat to cure. The resin and catalytic hardener are pre-mixed but curing does not occur because the catalyst is in an inactive form at room temperature. It only becomes reactive as the temperature is raised, usually in excess of 100°C. The higher the temperature, the faster the reaction becomes and hence shorter curing times of less than ten minutes can be obtained. Cure of the two-part adhesives can also be accelerated by heat."

Appellant in response to the first office action and the applied art added the term "two-part" to his claims and attempts to use the "ordinary meaning" in the plastics art to distinguish from the teaching references. Here he is attempting to persuade the Board that the scope of his claims is to a "two-part resin" defined by its conventional meaning used in industry and not the "two-part" resin as he disclosed throughout his specification. As set forth above, appellant has defined in his specification that to be a "two part resin" it only need to have and A-side and a B-side which includes both "one-part" and "two-part" resins commonly known in the art. One skilled in that art here is an ordinary bowler. Clearly, he would not be versed in plastics and the science surrounding polymers. Reading appellants specification, he would not conclude that his invention was drawn to a "two-part resin" as is conventionally used in the art of polymers. Instead, conveyed to him from appellant's specification would be that any plastic having an two parts, an A-side and B-side is required. Hence, for the purposes of this rejection, the broadest interpretation is, that the prior art regardless of whether it teaches a one-part or two-part resin as

commonly referred to in the polymer art, it meets the limitation of the claims where the resin used is comprise of more than one component.

Regardless of the interpretation of the scope afforded to the term two-part used in the instant claims, Shibantai is considered to most broadly disclose a "two-part" resin even in line with what one skilled in the art of polymers considers such to be. He discloses a "synthetic resin compound and glycol(s)" (col. 17, ln. 51). Appellant's conclusion on pg. 9, ln. 12 of the Brief that "Shinbantai do not require mixing" is in error. At col. 3, ln. 66, Sinbantai explicitly teaches "mixing with various synthetic resin materials...". Where he states that Shibantai is "limited to one-part thermoplastic resins..." he is misleading the Board. More aptly, he directly teaches (col. 7, ln. 56) that smell can be added to "epoxy resin coatings". Epoxy resin is a known "two part" resin. See evidence in the copy of Handbook of Reinforced Plastics, "Epoxy Resins", pg. 71, col. 1, ln. 20 where it shows that "cure may be established using materials classed as hardeners or curing agents". Appellant submitted NPL on 6/17/2003 to "Two-Part Sculpting Epoxies" further shows that epoxies are known to be two part polymers as called for by the claims.

With respect to Coffey, he suggests fragrances most broadly to "synthetic resins" (col. 1, ln. 11). He goes on to describe a preferred embodiment with "fluorocarbon resin" (col. 2, ln. 60). From U.S. Patent 4,314,004 to Stoneberg we see that fluorocarbon resins are formed by a reaction with a second part (col. 2, lns. 54-68) making them what can be considered a two-part resin. As such both Shinbantai and Coffey are not limited to only one part resins. Their disclosure is much broader and clearly suggest a two-part resin as called for by the claims.

Lastly, using a one-part or two-part resin have known properties with known advantages and disadvantage to one skilled in the art of polymers and resins can be formulated to be either one-part or two- part depending upon the requirements of the products to be made. For example, polyurethane can be either a one-part or a two-part polymer. See appellants NPL to "One and Two-Part Resin Systems" of 6/17/2003 for example. One skilled in the art would clearly expect a fragrance inclusion additive to work in both a one-part and a two-part resin, as understood in the polymer art, equally the same. This selection of a known material to take advantage of its known properties has been held obvious.

Obviousness of Claimed Invention Fairly taught.

First, a bowling ball that comprises a mass with a "two-part" resin as well as a polyol is old as admitted by appellant respectively on the bottom of pg. 2 of his specification and pg. 10, ln. 6 of his Brief. The base reference is applicant's own specification and what is admitted as old. The grounds for rejection recognizes that Shinbanai and Coffey do not teach the specific details of making a bowling ball. These teaching references are relied on for what they disclose about adding fragrance to products like a bowling ball made of two-part resins to make them smell better. The only thing missing from the prior art of bowling balls is the addition of fragrance to the resins used to make them. Both Shinbanai and Coffey fairly suggest adding fragrance to resins to impart smell to the product. Clearly one faced with the problem of wanting a bowling ball to smell more appealing would consider the teachings of these references.

As to claim 20, skill has to be presumed on the part of a person practicing the invention of Shinbanai. Known is that once the catalyst is added to polyol, there a "working time" for the resin is set when working with a two-part resin known in the polymer art. Mixing the fragrance into the polyol, the main fundamental ingredient thereof, prior to the catalyst does nothing more than what would be obvious to the skilled artisan. *KSR Int'l Co. v. Teleflex, Inc., No 04-1350 (U.S. APR. 30, 2007)*. Further, it is clear that the fragrance could be added to the polyol after the addition of the catalyst. However, it would need to be done such that it could be uniformly mixed and molded before polymerization were to begin. Clearly appellant is claiming nothing more than the use of known techniques that are inherent in the prior art.

As to claims 20 and 21-26, the removal of gas "trapped" in a polymer mixture is old and inherent in the art of plastics. Failure to do so results in an inferior final product made by the visibility of "bubbles" that art trapped after the product has fully cured. Surely applicant is not the inventor of removing trapped air or gas known throughout the plastics industry. See U.S. 6,525,125, col. 10, ln. 55 which discloses a resin for production of bowling balls and removing of gas bubbles under a vacuum at col. 11, ln 63. On pg. 8, [0032] of his specification, appellant admits to the use of a vacuum, as well as "any known techniques".

With respect to claim 21, Shinbanai discloses mixing fragrance inclusion compounds (col. 2, ln. 45) "with a synthetic resin coating" (col. 3, ln. 57) for "direct addition of perfume(s)... to a synthetic resin compound" (col 1, ln. 35). He discloses "epoxy resin" (col. 7, ln. 56) which is a broad category of known polyols. Polyol in the method of manufacturing of a bowling ball is old. This is admitted by appellant on his specification, paragraph [0004]. To further assist the Board in making its determination and to appropriately determine what is known in the art, the examiner has appended two websites that discuss the uses of polyol with respect to polyurethanes. Note <http://www.kosa.com/poly/specprod.htm> and <http://polyol.synair.com/AbOut%20Polyols.htm>, copies of which are appended to this examiners answer. As to claim 21, Webster's New World Dictionary defines "dissolve" as "to merge with a liquid". Shinbanai clearly teaches a fragrance that is to be "merged" with a liquid polymer

As set forth above, a catalyst is well known as being used with polyols to cause polymerization. The use of a catalyst as called for in claim 23 is not new to the art of plastics.

The use of isocyanates as called for by claim 24 is old. The Boards attention is drawn to pg. 5 of copies the *Handbook* appended to this Answer. As mentioned previously in the Answer, they are mostly known for having a "foaming" affect on plastic compositions.

Motivation to Combine

As set forth in the final office action sufficient motivation to combine the teachings of Shinbanai and Coffey with bowling balls two-part polyurethane bowling balls, admittedly old and well known, in order to give them a better smell. Where both polyurethane bowling balls are known in the art and "fragrance inclusion compounds" for products made of a resin such as polyurethane, it is clear that appellant did not "invent" adding a fragrance to a bowling ball. Instead he took know materials such as a fragrance inclusion compound and applied it for its intended purpose of imparting smell to a final product.

The controlling principles of the Law of Obviousness here resides in *KSR Int'l Co. v. Teleflex, Inc.*, No 04-1350 (U.S. APR. 30, 2007) and not in whether there is an explicit teaching suggestion or motivation as implied by appellant. Here, in line with *KSR*, we have a clear cut situation before the Board where appellant's improvement is nothing "more than the predictable use of prior art elements according

to their established functions” and merely combined prior art elements according to known methods to yield predictable results. Clearly, fragrance inclusion products and methods that have been applied in the art to be known to work on other polymer resin products would be expected to work on a bowling ball made of similar polymers. The level of ordinary skill necessary to recognize the results is low. Here one can see of record no new or different function of the bowling ball of the instant invention and the results of adding fragrance to a polymer in a bowling ball give the predictable results of having the bowling ball smell according to the fragrance added.

KSR further supports the examiner’s position where appellant has merely used known techniques of adding fragrance to polymers used in articles made of plastic to improve to improve similar articles made of plastic, such as a bowling ball. The addition a fragrance inclusion, such as that taught by Shinbanai and Coffey, into a plastic product would have clearly been well within the skill of one of ordinary skill in the art of plastics. The results of making any plastic product that such a fragrance is applied to smell better is considered expected and predictable. Here we have the situation where appellant has done nothing more than applied known techniques of including a fragrance into a plastic resin product to yield a predictable outcome with only common tools of the trade.

Here the rejection does not suggest to “modify the teachings of Shinbanai and Coffey” (Brief, pg. 12, ln. 3). The rejection suggests modifying known two-part polyurethane bowling balls, admitted old by appellant at the bottom of pg. 2 of his specification, using the products and techniques known in the art as suggested by Shinbanai and Coffey. One would clearly recognize that known techniques for imparting a fragrance in plastic products would yield the same results in other products made of similar polymer materials.

In order to make a rejection tenable, there is no requirement that one skilled in the art would need to be aware of “any demand for scented bowling balls” (Brief, pg. 12, ln. 15). Here the scenting of the bowling ball is nothing more than a novelty as is recognized in the art of adding a scent to other products. One wishing to add the same novelty of smell to a product such as a bowling ball would surely consider how this novelty was practiced in other articles made of similar polymers.

In the middle of pg. 13, appellant asserts that the fragrance added to the bowling ball yields unpredictable results by increasing friction and the "hooking ability" of the ball. First, the hooking potential of a ball is controlled by the design features of the ball such as the shape, weight design and placement of core material and the type of coverstock used on the ball. There is no evidence that it is merely the addition of fragrance that would give the ball any better performance and that the performance may not be attributed to another feature of the ball. In the article of record provided with the affidavit of 6/28/05, *Fragrances Add Some Zest to Bowling Balls*, appellant appears to point to a quote by "Steve Kloempken, the company's technical director, says computer tests indicate that the aromatic chemicals give Storms balls a bit of extra hook". However, this statement is not substantiated by any evidence of record such as the computer test to which he refers. Here appellant has not shown where identical balls, with the exception of one without fragrance and another with, will perform any different. Lastly, upon review, nowhere in the specification does it mention an increased hooking potential.

Secondary Considerations

Appellant argues that "the commercial success of Storm's scented bowling balls may be attributed to the incorporation of the fragrance therein" (bottom pg. 14). The fact that the commercial success MAY only be attributed to the added fragrance is the reason that the secondary considerations have been unpersuasive. The declarations provided only contained conclusions without establishing a nexus between those conclusions with and any supporting evidence to the scope of the instant claims. In essence, they amount to an opinion that is considered of limited probative value with regard to rebutting a prima facie case. *In re Grunwell*, 609 F.2d 486, 203 USPQ 1055 (CCPA 1979); *In re Buchner*, 929 F.2d 660, 18 USPQ2d 1331 (Fed. Cir. 1991). The burden is upon appellant to show a clear nexus between the commercial success and the claimed invention which has not been done. The Federal Circuit has acknowledged that applicant bears the burden of establishing nexus, stating:

In the ex parte process of examining a patent application, however, the PTO lacks the means or resources to gather evidence which supports or refutes the applicant's assertion that the sales constitute commercial success. C.f. *Ex parte Remark*, 15USPQ2d 1498, 1503 ([BPAI] 1990) (evidentiary routine of shifting burdens in

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civil proceedings inappropriate in ex parte prosecution proceedings because examiner has no available means for adducing evidence). Consequently, the PTO must rely upon the applicant to provide hard evidence of commercial success. In re Huang , 100 F.3d 135, 139-40, 40 USPQ2d 1685, 1689 (Fed. Cir. 1996). See also GPAC, 57 F.3d at 1580, 35 USPQ2d at 1121; In re Paulsen, 30 F.3d 1475, 1482, 31 USPQ2d 1671, 1676 (Fed. Cir. 1994)

The examiner has considered the Declaration of John Chrisman and has determined that the commercial success of the Storm bowling ball has not been shown to be linked to the claimed invention. First, the "scent" has been referred to as a "gimmick" which is in all likelihood linked to a heavy advertising and promotional budget. Nothing of record shows that the increased sales in 2001 for Storm was not linked to greater promotion or endorsements of its products or other products popular in its product line rather than to the scenting of the balls itself. Non-obviousness is not shown by a brilliant marketing strategy that includes press releases and recognition from the novelty of the ball. Second, the balls of Storm sell because they perform well. It is the overall design and performance of the ball that has resulted in its success and not the mere addition of a fragrance. Examiner is not convinced that top bowlers would buy the Storm ball merely because it smells good. It the top performance characteristics of the ball that is attributed to the success of the company and the sales of its balls. Moreover, the article in eMediaWire state that the balls of Storm were discounted with a "savings of over 30%". Clearly discounting sales can lead to the commercial success of a product. Lastly, it has further not been shown that Storm products are not being priced cheaper than the competition or with buying incentives that account for the percentages of growth in sales being claimed.

Where appellant alleges a "great deal" of commercial success even though the balls have been sold for 10% more than comparable balls, he has not qualified what is considered to be a "great deal" and a "comparable balls". Note that he did not say that the ball sold for 10% more than for "identical" unscented balls. Clearly, colors, advertising, discounts, better performance, new endorsements and the like can easily account for an 10% increase in sales price. Likewise, appellant does not qualify to what "30% share of their market segment" pertains. Is this the market segment of identical unscented balls? Do they even offer identical unscented balls? Clearly, no nexus has been established and the evidence of secondary consideration is unpersuasive.

(b) SHINBANAI, COFFEY AND ANDERSON

Appellant argues that the rejected claims are allowable base on their dependency of the claims argued above. Examiner's position is set forth above and no further comment is deemed necessary.

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner's answer.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,

/William M. Pierce/ Primary Examiner 3711

Conferees:

/Marc Jimenez/ TQAS TC 3700

/Gene Kim/ Supervisory Patent Examiner 3711



HANDBOOK OF REINFORCED PLASTICS

of The Society of The Plastics Industry, Inc.

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Chapter 1-1

WHAT ARE REINFORCED PLASTICS?

A complete understanding of the field of Reinforced Plastics is almost impossible without a basic knowledge of the plastics industry as a whole. Briefly speaking, plastics are materials, generally of high molecular weight and of indefinite molecular complexity, whose form and/or properties may be transformed into useful shapes or articles by the techniques of applying heat, pressure, or other manufacturing procedures. Still joining with a broad brush, we may divide plastics into two general categories, the thermoplastics and the thermosets.

Many analogies have been used to illustrate the differences between these two groups, none of which hold completely. For example, thermoplastics have been compared with candles, while thermosets have been compared with eggs. That is, a candle (thermoplastic) may be shaped, melted, reshaped, and so on, until the molder has exhausted his possibilities. The egg, however, having once been cooked hard, cannot be "uncooked." This is the picture given to the layman, and it suffices as a general method of differentiating between the groups.

But for someone who wants to design or manufacture articles from these wonderful materials, so simple a division is not sufficient. Particular properties of each material must be known, so that intelligent use may be made of it and, most important to the plastics industry, misuse may be avoided.

Following is an alphabetical list of currently available plastic groups and a brief examination of each with respect to its properties and uses.

Acetal Resins

This resin, a thermoplastic, was introduced commercially in 1929. According to its producers, it is said, among the good fatigue properties, is excellent and tough, with low moisture

sensitivity and high solvent resistance, offering excellent electrical properties. Melting temperature is 400 to 440°F, heat distortion temperature 385°F. When molded, it has a tensile strength of 10,000 psi, a compressive strength of 18,000 psi, and a flexural strength of 14,100 psi. At room temperature, it is highly resistant to common solvents. Acetal resins may be molded by injection or extrusion into many shapes, including rods, sheets, and tubes. Their uses encompass many fields, from pump impellers and havo-over wheels to instrument casings and slide fasteners for clothing.

Acrylics

These widely used materials are probably best known by the trade names given by their major producers: "Plexiglas" (Rohm and Haas), "Lucite" (du Pont), and "Perspex" (Imperial Chemical Industries). They are, for the most part, methyl methacrylate polymers used as sheets, molding powders, in exchange resins, and textile fibers. Depending upon the molding process, they are handled at temperatures between 300 and 500°F. They are classified as thermoplastics, and have tensile strengths of about 7000 psi, compressive strengths in the 12,000 to 18000 psi range, and flexural strengths ranging from 13000 to 17000 psi. Acrylics are used for glazing material, for automotive parts, for many plates, knobs, dish, street lights, and a host of other applications.

Amino Resins

While this designation may be rather misleading, the more widely used members of the amino family, urea-formaldehyde and melamine-formaldehyde resins, account for millions of pounds of annual use in such diverse areas as appliance housings, dinnerware, buttons, electrical devices, plywood, and the paper industry.

They are thermosetting and have excellent resistance to heat and moisture. These properties account for many of their uses as surface finishes, as bases for baking enamel, and in table-top materials.

Alkyd Molding Compounds

These thermosetting compounds are based upon polyester resins, modified to provide easy handling and long storage life. As produced, they are available in three major forms: putty, fiber-reinforced, and granular. Compared with other thermosetting materials, their physical properties are not high, especially in tension. They do, however, have excellent electrical properties and dimensional stability so that, with proper design, many good applications are apparent. The greatest volume of alkyd molding compounds finds its way into the field of electrical components, such as switchgear, motor housings, circuit breakers, etc.

Cellulose

A wide variety of cellulose compounds is available in the thermoplastic molding field. These include ethyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate, and cellulose nitrate. Probably the best known of the cellulose films is cellophane, which is widely used as a packaging material and barrier against moisture and gases. Cellulose acetate, however, is not so readily soluble in cold water. Their wide diversity of chemical formulas makes them useful in such applications as automobile components, photographic film, and appetite-depressant tablets.

Epoxy Resins

Originating as commercially available materials about 1940, these thermosetting resins are rapidly assuming a major role in the fields of reinforced plastics, surfacing and adhesives. They have excellent resistance to attack by moisture and corrosive chemicals, and provide extraordinarily high strength to laminates and molded parts. The aerospace industry has used epoxy to great advantage in areas where other materials have provided unacceptable properties. For example, laminar and tensile moduli of two and three times those commonly developed with polyester laminates have been reported.

Ethylene Polymers

Currently being produced in the billion-pound-per-year area, polyethylenes in its various grades is probably the most widely used of all thermoplastic materials, if not of all plastics. Available in three general grades, the low, medium, and high-density polymers, polyethylene is used in injection molding, film, sheeting, extruded laminates, pipe, coatings, fibers, tubes, blow-moldings and numerous other applications. As an example of its diversity, it is found in desirable bottles for nursing babies and in cables for shielding nuclear reactors. Its mechanical properties are relatively low, as is its resistance to heat.

Fluorocarbons

An unusual group of thermoplastic materials is included under the heading of fluorocarbons. They are relatively new in the plastics field but have properties of great interest and potential. The major characteristics of interest include excellent thermal resistance and almost complete resistance to attack by solvents. Chemically, they are practically inert. They are available as molding powders and in extruded forms. When added, they have remarkable dielectric properties, exceptional resistance to solvents, good toughness, excellent resistance to weathering, and zero absorption of moisture. Applications include insulating coatings, extrudates, injection moldings, compression, and transfer moldings for laminates, electrical parts, sheet, film, printed circuits and temperature-resistant seals.

Furans

Most of the resins with which the plastics industry works are derived from petroleum and its by-products. One group, however, originates in agricultural materials. These resins, the furans (or furans) are the result of reacting furfuryl alcohol, a vegetable derivative, with various catalysts, aldehydes, ketones, dimethyl urea, and other reagents to produce resins, polymers, and plasticizers, coatings, impregnants and other plastics. The thermosetting resins thus developed are liquid until polymerized. The furans provide protective coatings for metals, could contain, and chemically resistant table-top materials.

Isocyanates

Strictly speaking, the isocyanates are not resins. They are, rather, a group of materials which, when reacted with one of a number of resin products, the family of products known as isocyanates, have tremendous resistance to heat and moisture. These compounds have tremendous resistance to heat and moisture, excellent adhesion, and form a tough, flexible polymer. They are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint. Isocyanates are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint.

Polyester Resins

Still another one member of the thermoplastic family of resins is the polyester group. Its primary application stems from its excellent dimensional stability under varying conditions of temperature and humidity. High (200 to 200°F) heat resistance, good electrical properties and high impact strength. Chemically, the polyester resins consist of long-chain molecules joined together by ester bonds. They are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint.

Polyesters

This family of thermosetting resins is the basis for the entire Reinforced Plastics industry, and much more emphasis will be placed upon their properties and processing in later sections of this handbook. Essentially, a polyester is the result of the reaction of a diisocyanate with a glycolic alcohol, but the variations of this reaction encompass many basic materials, resulting in resins with widely diversified properties. In general, however, the important characteristics of polyester resins include good electrical and physical properties, easy handling, solubility in many solvents, and good dimensional stability. They are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint.

Polyolefins

Chemically classed among the simplest of polymers, the group includes polyethylene and polypropylene, which account for a high percentage of the volume of the plastic materials available in three general classifications: low density, medium density, and high density. They are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint.

Polyurethanes

These thermoplastic resins are better known as urea, and the applications run the gamut from antistatic and household appliances in the industrial field through sporting goods, such as football helmets, to textile fibers for use in fibers. There are at least half a dozen types of urea, based upon as many chemical reactions, but the general family is derived from the reaction of various diamines with diisocyanates. They are used in a wide variety of applications, such as coatings, adhesives, and as casting materials for various plastics. They are also used in the production of rigid foams, frequently bonded to plastic, provide excellent laminates in reinforced plastics. Urethane coating materials are used for example, in the production of paint.

England, first suggested industrial applications for the reaction products of phenol and formaldehyde, the so-called "77" resins. For many years that remained the commonest of the thermosetting plastics. Today, they are still of considerable importance, but they are not the only plastics. Today, there are the last fifty years, and particularly since 1920, numerous plastics have been made, and plastics now comprise nearly half of all plastics. Examples of thermosetting plastics include phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde. All these materials cure through a condensation reaction during which a water molecule is removed, often water or steam, is evolved. These by-products can cause blisters in the molding, and it is the prevention of such blisters which makes the use of high pressure necessary.

Unstressed polyester resins—or polyester resins as they are usually called—are thermosetting, but they have the great advantage that they cure through an additional polymerization reaction and do not evolve volatile by-products in the process. They can therefore be molded at low pressures, frequently only at pressure sufficient to keep the molding in contact with the mold, i.e., contact pressure. Their development made it possible to mold shapes of almost unlimited size at an economic price, which had previously been impossible.

When used alone, however, polyester resins are not strong or tough; but in combination with certain reinforcing materials, mainly some form of glass fiber, they exhibit properties which make them suitable as structural materials of considerable load-bearing capacity.

Although most thermosetting plastics are reinforced with fibers either in powder or fibrous form to give them improved mechanical properties, the term "reinforced plastic" is used almost exclusively to describe glass-fiber Reinforced Plastic, of which the overwhelming part consists of glass-fiber reinforced polyester resins.

Some of the reasons which make polyester resins and glass fiber such an excellent combination for reinforced plastics are:

- Polyester resins are liquid and will therefore flow and impregnate glass fiber with little or no pressure.
- Glass fiber is one of the strongest known materials and because it is glass, will not deteriorate even after long periods of time.
- Glass fiber is easily crushed. This makes it unsuitable for high-pressure molding techniques. Since polyester resin can be cured with little or no pressure, glass fiber

is therefore an ideal reinforcing material for it.

- Fully cured polyester-glass-fiber moldings and laminates have excellent physical properties and better strength-weight ratios than many metals. Their good electrical properties and resistance to corrosion also make them suitable for many specialized applications. The manufacture of moldings for aircraft was, in fact, the first large-scale application of polyester-glass-fiber structures.

Various methods have been developed for the successful molding of glass-fiber reinforced polyester resins. They are fully discussed in later chapters, but mention is made here of the two most important techniques.

- Continuous molding. External pressure is not required. This method is ideal for small-to-medium-sized runs of large articles, such as vehicle bodies and boat hulls.
- Hot low-pressure molding. More equipment is needed, but the molding cycle is shorter. It is used for the production of small to medium-sized articles.

Polyester resins are cured by the addition of chemical compounds which control the polymerization reaction. These are:

- Quinols (sometimes called hardeners or initiators)—to initiate polymerization
- Accelerators (sometimes called promoters)—used in conjunction with catalysts to enable polymerization to take place without the use of external heat.

Other auxiliary materials which are frequently used are:

- Mold release agents—to facilitate separation of the molding from the mold.
- Flow-control agents or flowers—flow-control agents to provide special properties or to extend the resin.

Reinforced plastics have frequently been made for Reinforced Plastic, as indeed, for many other materials. Every material has its own peculiar properties and its own specific applications. The fact that Reinforced Plastic can be successfully applied to a wide variety of uses does not mean that they can be used indiscriminately to replace other materials. It would be foolish to pretend that Reinforced Plastic has no limitations. To help designers and fabricators to decide whether polyester-glass fiber is a suitable material for a particular

application, the advantages and disadvantages may be summarized as follows:

Disadvantages:

- All fabricating processes are slow by comparison with those used for pressed steel or sheet metal.
- Cost of resin and glass is comparatively high. However, this is frequently offset by less costly equipment and by less highly skilled labor.
- Mechanical and other properties of constant molded components tend to be inconsistent.
- The rigidity of Reinforced Plastic is not very high, when compared with that of many metals.

Advantages:

- Large complex shapes can be molded easily and cheaply.
- Reinforced Plastic offers a greater freedom in design than most other materials.
- Reinforced Plastic has a high strength-weight ratio.
- Reinforced Plastic is extremely resistant. They do not dent like metal.
- Reinforced Plastic has good weathering properties. They do not corrode, are resistant to many chemicals and to mold and fungus attack.

Reinforced Plastic should be seriously considered for production applications when the following conditions are involved:

- The expected production run will not exceed a limited number of parts. Depending on the size and complexity of the design, this number may be as small as a dozen or as great as 50,000. However, cost of tooling and mold subsequent operations should be considered and compared with those for similar operations in other materials.

Reinforced Plastic when favorable cost and schedule ratios are apparent. Reinforced Plastic should be selected provided that no compromise in quality and/or performance is involved thereby.

(2) A complete assembly in competing materials may be replaced by a single molding in Reinforced Plastic. Frequently, it is possible to mold complex contours in one operation, when a mold part of identical or similar shape would require fabrication and assembly from several components. Reinforced Plastic demonstrates consistent advantages in this respect, in

WHAT ARE REINFORCED PLASTICS?

10

that they afford considerable savings in finishing labor.

(3) Tooling for alternate materials would be usually expensive or time-consuming. Because of the processes used in production of Reinforced Plastics, tool and mold requirements are usually much less stringent and expensive than those for metal. Consequently, cost may be as little as 10% of that used for metal. Consequently, tooling schedules are frequently measured in weeks, rather than months.

(4) Complex or intricate detail is required in the molded part. Partly by nature of the materials and processes involved, Reinforced Plastics will reproduce fine details of surface design and texture. The only reasonable limitation is that imposed by the effort expended in preparing the mold surface.

(5) Environmental conditions make performance and/or service life questionable. Where exposure to unusual temperatures, chemical attack, damp atmosphere, corrosion, or other degrading influences may be expected, investigation of Reinforced Plastics as a material for application should be seriously undertaken. Properly used, they provide long and satisfactory service life under conditions which would rapidly cause failure of conventional materials. Often, costs which might appear prohibitive as far as competitive materials are concerned are completely justified when compared in the light of projected service life, replacement expense, machine "down time" and similar factors.

(6) Weight and/or strength retention are problems. On a strength/weight basis, Reinforced Plastics will usually outperform most competitive materials. This is almost always an advantage in air-borne applications, and cer-

tainly is a favorable factor in most other forms of transportation, where prime concern must be selected on the basis of weight of cargo. In the area of strength retention, it is a fact that Reinforced Plastics maintain their ability to carry design loads at temperatures far below, or in excess of the temperatures at which metals, for example, will perform. They are not inhibited by exposure to cryogenic conditions, but actually improve their properties. And, at elevated temperatures where metals would become unserviceable, the plastic materials continue to perform adequately with little, if any, loss of strength.

(7) Impact damage is probable or possible. Reinforced Plastics do not deform when broken. When ultimate impact strength is exceeded and fracture occurs, repairs may be effected by simply making the fracture edges and bonding or patching. No dents or bumps need be removed. A typical example here is an automobile fender or machine housing, which is subject to rough usage.

(8) Color is required. Again, by virtue of the processing techniques used, it is customary to include dyes or pigments in the molding. This provides uniform properties through the molded wall. No painting is necessary, damage from chipping or abrasion is eliminated, and good performance is insured. Finishing costs are, of course, often avoided, since final surface treatments are unnecessary.

(9) Frequent variations or design changes are expected. As discussed earlier, tooling is often not complex, and minor changes can be made rapidly. When major changes are involved, replacement of tools is not nearly as costly as with competitive materials.

SECTION II

Resins, Catalysts, Promoters

References

No.	Author(s)	Title or Periodic	Vol.	P. pub.	Year
1		"Polyester Handbook," Scott Bader & Co., Ltd.			1961
2		Molded Fiber Glass Body Company Presentation to Body Engineers' Society Meeting			1960

Chapter II-1

POLYESTER RESINS

POLYESTER RESIN MANUFACTURE

Most of the raw materials used in producing Reinforced Plastics are themselves finished products. Resins are synthetically produced from materials which, in turn, do not occur in nature. Glass fibers and other reinforcements are derived from natural materials which have been reprocessed. Only the filling materials are comprised of naturally occurring substances. While this dependence upon "synthetics" may have the disadvantage of high raw-material cost, it has nevertheless made possible a unique and continually growing stream of products and strong but flexible filament with a weak but continuous liquid-thin-benzene-soluble matrix.

Resins in general are discussed in this section, and a separate chapter is devoted to each of the following types: polyester, phenolic, epoxy, silicone, acrylic, and unsaturated, including melamine, furan, special thermoplastics, and inorganic types. In each resin chapter, the same general outline is followed, consisting of a description of general resin manufacturing procedures and control, resin properties, fields of usage and typical formulations, and, finally, resin chemistry and methods of catalyzing and promoting the cure.

Polyesters for use in Reinforced Plastics are available primarily in liquid form, although unsaturated and solid resins are available for specific purposes. The liquid resins are available in room-temperature viscosities ranging from very thin to asphaltlike; this is fortunate because the best properties of both resin and reinforcing agent are brought out by making the combination, the various viscosities being dictated by the end molding requirements. Also, the entire amount of monomer (reactive thinner) added to the resin becomes a part of the cured resin

structure during polymerization (hardening or solidification due to chemical action).

Polyester resins result when certain organic acids or acid anhydrides, termed di- or poly-carboxylic acids (two or more carboxyl (COOH) groups per molecule) are reacted with a specific class of organic alcohols termed polyols (two or more hydroxyl (OH) groups per molecule). Such a reaction is termed an "esterification" process. An ester is the organic equivalent of the inorganic salt derived from the chemical reaction between an inorganic acid and base.

Equipment for large-scale production of polyesters consists of a 14 in. to 1½ in.-wall stainless steel tank vertically aligned, approximately 8-ft. diameter and 10 to 12 ft. high (for 20,000-pound batch), with dished top and bottom, and 3 or 4 sealable entry ports or manholes in the top dome. A space allowance of 10 to 20% over batch size is made for head room in the top dome.

An 8 to 10 in. or larger diameter driver and 40-hp motor for agitation are mounted from the top dome so that the driver shaft extends vertically and is bearing-mounted at the bottom of the kettle; and driver blades are located at two or three levels along the shaft. A large steam- or hot water-jacketed condenser unit is also mounted from the top dome, with return piping and drainage to the atmosphere or a floor drain. The condenser must be occasionally steam-cleaned or blown out to prevent clogging.

Heating means are provided by a jacket around the outside kettle wall. The jacket is piped to a boiler and heat-exchange unit where heat is transferred to a high heat-capacity liquid (glycerol and diphenyl acids) which provides a medium of the required high reaction temperatures without need for accompanying high pressures. Premixed gas and air combustion units and electricity are also used for heating in some kettle operations.

cooling with facilities for creating a negative pressure, and an inert gas (CO₂ or N₂) blanket. In a brief follow-through of the processing of a polyester resin production batch, the steps are as follows:

(1) Acids or anhydrides and glycols are accurately weighed, as inert gas is introduced by bubbling from the bottom and an inhibitor is added. With mild heating, the acids rapidly react in the glycol; some initial foaming occurs.

(2) A stir, stoppage heating cycle is followed over a 2 to 4-hour period, gradually raising the temperature to the final reaction temperature. Acid unit is used and viscosity control measurements are made during this period. Water is liberated and removed by the vacuum.

(3) The stir is kept at 410°F (210°C) until the acid number is less than 50, or reaches the desired value (which may be lower), and the viscosity is within predetermined limiting values. Acid time is determined.

(4) If satisfactory within specification, the mix is cooled to 210°F and transferred to the thinning bottle. Monomer is added to maintain usable viscosity and impart other desired properties required for handling and ultimate end use.

In a typical polyester producing plant, the reaction-kettle heating station is on the third-floor level, the measure to the thinning bottle on the second-floor level, and the thinning-bottle unloading station at the ground-floor level. In a well-designed modern battery, adequate open space is allowed around the kettles at each level to facilitate movement of materials and personnel, and both the reaction and thinning units are independently suspended on separate scales with live-pond gradations for accuracy in batch

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res. Other, final gel time, and other pertinent properties are determined. The complete production cycle requires a minimum of approximately 8 hours.

It may be of interest to illustrate the over-all production efficiency of a polyester-producing unit. In producing what might be termed a representative or standard polyester resin batch, 1 mole or 1 equivalent of acid requires 1 mole or 1 equivalent of glycol for complete esterification. Hence, to produce a general-purpose, solvent-type resin, 1 mole of maleic acid anhydride (MW = 98) and 1 mole of polybutene acid anhydride (MW = 140) would react with 2 moles of diethylene glycol (MW = 106), allow minimum of 5% excess and 1 mole of water (MW = 18) would be produced for each mole of anhydride. Stoichiometrically:

maleic anhydride + polybutene acid anhydride + 2 diethylene glycol
 98 parts 140 parts 213 + 11 parts (1)
 = ester + water
 429 parts 50 parts

A portion of the excess glycol remains as part of the polyester, and the water is removed by the condenser, so that the batch yield is (theoretically):

$$\frac{429}{429} \times 100 = 92.5\%$$

In producing the complete batch, including monomer, if 55% excess monomer were added in the thinning bottle to produce resin with a working viscosity of approximately 20 poise, the batch and loss figures would be represented as:

Reaction ingredients	Input	Output	Loss
Reaction ingredients	468 parts	429 parts	39 parts
Kettle ingredients	above output	100 parts	100 parts
Losses	100 parts	100 parts	100 parts
Total	468 parts	529 parts	529 parts
Per cent yield, complete batch			94.1%

RESIN PROPERTIES

Of the total polyester output, liquid resins represent the largest sales volume, although some solid polymeric resins are produced. Certain specialized tests are performed on resins in the liquid state both during and following manufacture to make certain that the reaction has progressed satisfactorily, and to define other functions for control purposes. Other tests are performed on the solid polymeric resins (unmodified) to indicate its probable behavior in the end use. Polymeric resins may be evaluated by the same group of tests where applicable.

About all tests involved have some value to the end user by helping him understand, evaluate, differentiate, or select resins to suit his own requirements. Performance properties of modified

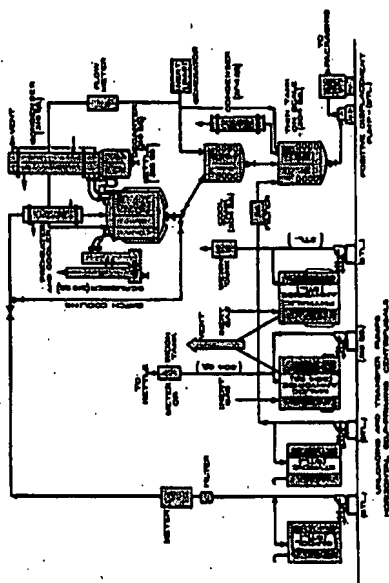


Figure 11-1.1. Typical plant for polyester resin production. (Courtesy Monsanto Chemical Company)

parts are discussed in Section VIII. However, the particular group of tests described in this section applies only to unfractionated resins. ASTM or other pertinent test methods are referred to when necessary.

Tests on Liquid, Unfractionated Resins

Acid Number. The acid number is used to determine the progress of the esterification reaction. The excess glycol mentioned above is desirable in the batch to reduce the acid number before the reaction proceeds too far. During an esterification reaction, the acid number usually is first determined at a value of 80 and then further reduced to a value between 50 and 8 in the finished resin. Hence, it is also an indication of product uniformity for batch-to-batch control of a given resin.

The acid number is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acids in 1 gram of the resin. In making the laboratory determination, a 50:50 alcohol-benzene reagent is made up, and 3 or 4 to 10 grams of resin (10 grams required for higher acid numbers) are accurately weighed into 50 ml of the reagent. A small amount of neutral acetone may be necessary to make in dissolving some resins. The mixture is cooled and titrated with 0.2N KOH in methyl alcohol to a pH of 8.5 to 9.0 using bromothymol blue indicator.

Calculation: Acid No.

$$\frac{\text{ml KOH} \times N \times 56.1}{\text{sample weight (in grams)}}$$

Hydroxyl Number. Another function, the hydroxyl number, is related to the acid number, and is sometimes used to advantage in describing the properties or in checking the quality of a polyester resin. Hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1.0 gram of the resin. It points up the low molecular weight content of the resin, and will give an indication of whether or not excess glycol was added to the finished resin to speedily adjust its finished acid number prior to shipment. Procedure for determining hydroxyl number is lengthy, but may be found in standard analytical works.

Viscosity. Although there is chemically an optimum monomer content or dilution for a given amount of resin solids, monomer additions

5 to 8 parts resin prevents rundown from a vertical surface during the time the resin remains in the uncured state.

The third aspect of fluid-state viscosities concerns rheology, which may be defined as fluid solidification of certain thixotropic fluids caused by a slow, repeated circular motion.

Of the several viscosity determination test methods applicable to polyester resins, the two most commonly used are:

(1) The most accurate rotating spindle viscometer, in which shear is induced by a cylinder or disc rotated at three separate speeds, with the liquid resin at the required temperature, and

(2) Rate of bubble rise, by which the unknown (sample) is in a 107 X 116 mm corral glass tube (approximate dimensions) is inverted, and the rate of bubble rise matched with that for known liquid standards at the same (77°F) temperature (ASTM D154 and D 1-56). The method has an accuracy of ±5%.

Figure 11-13 shows a series of bubble viscometer tubes, and Table 11-13 presents a table of the bubble viscometer linear designations correlated with corresponding viscosity units in Stokes.

In the high-temperature range (to 400°F), viscosity measurements may be made on unfractionated or unfractionated resins (rotating spindle method) to obtain a curve which will be of value in determining efficiency of hot-dip applications. Various resin compositions, of course, exhibit different softening points and viscosity curves in this upper-temperature range.

The viscosity-temperature variation for a characteristic polyester containing approximately 80% styrene monomer with a 79°F viscosity of 20 poise (St.) will be ±1.7 to 2.0 poise for each degree F rise or decrease (reversibility) in temperature. Hence, it can be seen that shear, curd viscosity control is important in making viscosity determinations.

The change induced by styrene monomer addition to the resin held at room temperature amounts to approximately minus 1.0 poise for each 1% of styrene added, and vice versa.

In addition to governing resin usage, viscosity

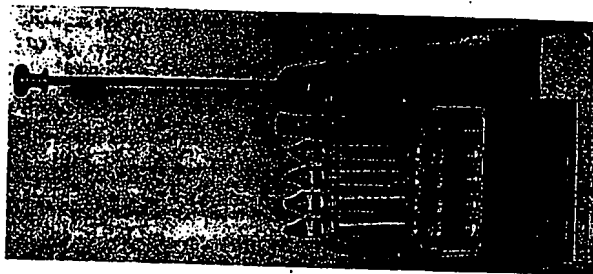


Figure 11-13. Equipment for viscosity determination by bubble viscometer. (Courtesy Corning Laboratories, Inc.)

measurement is also useful as a batch-to-batch control for both resin manufacturers and user. A plot of acid numbers and viscosity is usually made during the course of the esterification reaction. (See Figure 11-12.)

Specific Gravity and Shrinkage. The specific gravity of a resin is the ratio of the weight of a unit volume to the same unit volume of distilled water (at 72.4 ± 2°F). For liquid resins, the specific gravity is most aptly determined using a 25 ml wide-mouth Hubbard-Cornish pycnometer for weighing water and resin at

* Brookfield Model RVT; Brookfield Engineering Laboratories; Stoughton, Mass.
† Gardner-Holm Bubble Tubes (Listened A, to A.); Gardner-Holm Laboratories; Berkeley, Md.

TABLE II-1.1. Comparison of Bureau Viscosity Measurements with Viscosity in Boxes at 177°

Batch No. Letter Reference	Apparent Viscosity, Poise
A ₁	0.0005
A ₂	0.001
A ₃	0.0015
A ₄	0.002
A ₅	0.0025
A ₆	0.003
A ₇	0.0035
A ₈	0.004
A ₉	0.0045
A ₁₀	0.005
A ₁₁	0.0055
A ₁₂	0.006
A ₁₃	0.0065
A ₁₄	0.007
A ₁₅	0.0075
A ₁₆	0.008
A ₁₇	0.0085
A ₁₈	0.009
A ₁₉	0.0095
A ₂₀	0.01
A ₂₁	0.0105
A ₂₂	0.011
A ₂₃	0.0115
A ₂₄	0.012
A ₂₅	0.0125
A ₂₆	0.013
A ₂₇	0.0135
A ₂₈	0.014
A ₂₉	0.0145
A ₃₀	0.015
A ₃₁	0.0155
A ₃₂	0.016
A ₃₃	0.0165
A ₃₄	0.017
A ₃₅	0.0175
A ₃₆	0.018
A ₃₇	0.0185
A ₃₈	0.019
A ₃₉	0.0195
A ₄₀	0.02
A ₄₁	0.0205
A ₄₂	0.021
A ₄₃	0.0215
A ₄₄	0.022
A ₄₅	0.0225
A ₄₆	0.023
A ₄₇	0.0235
A ₄₈	0.024
A ₄₉	0.0245
A ₅₀	0.025
A ₅₁	0.0255
A ₅₂	0.026
A ₅₃	0.0265
A ₅₄	0.027
A ₅₅	0.0275
A ₅₆	0.028
A ₅₇	0.0285
A ₅₈	0.029
A ₅₉	0.0295
A ₆₀	0.03
A ₆₁	0.0305
A ₆₂	0.031
A ₆₃	0.0315
A ₆₄	0.032
A ₆₅	0.0325
A ₆₆	0.033
A ₆₇	0.0335
A ₆₈	0.034
A ₆₉	0.0345
A ₇₀	0.035
A ₇₁	0.0355
A ₇₂	0.036
A ₇₃	0.0365
A ₇₄	0.037
A ₇₅	0.0375
A ₇₆	0.038
A ₇₇	0.0385
A ₇₈	0.039
A ₇₉	0.0395
A ₈₀	0.04
A ₈₁	0.0405
A ₈₂	0.041
A ₈₃	0.0415
A ₈₄	0.042
A ₈₅	0.0425
A ₈₆	0.043
A ₈₇	0.0435
A ₈₈	0.044
A ₈₉	0.0445
A ₉₀	0.045
A ₉₁	0.0455
A ₉₂	0.046
A ₉₃	0.0465
A ₉₄	0.047
A ₉₅	0.0475
A ₉₆	0.048
A ₉₇	0.0485
A ₉₈	0.049
A ₉₉	0.0495
A ₁₀₀	0.05

This figure is a valid expression of volume change only, because a polyester resin gels prior to any evidence of chemical polymerization reaction (such as exotherm). Another method developed at Purdue University for testing shrinkage of filled plastics from liquid (estimated) to hardened or cured state may be applicable.

The volume change is not an accurate statement of the thermal expansion of a polyester resin, because of a limitation, however, and the values for this property should be determined with a dilatometer (ASTM D30 and D373).¹⁰ The term "polymerization" or "chemical change" (irreversible), which "normal" shrinkage (or expansion) refers to that induced by temperature changes (reversible).

Water Content. Due to the fact that the original esterification reaction is reversible, a re-adsorption of water under favorable conditions will convert a polyester into its original monomers. At room temperature, polyester resins will actually absorb several per cent of water by weight. Therefore, a maximum water content specification of 0.1 or 0.15% by weight should be maintained for finished polyester resins for several reasons, chiefly (1) to make certain that the esterification has proceeded as required and that the condenser has not malfunctioned, and (2) that no mechanical failure of the piping system has occurred. Permitting water to permeate the resin. Water, when mixed with water, will cause delay and irreversibility of the resin gel time (see pp. 14, 22, and 20). Acid also will weaken an ester bond, and, particularly due to formation of steam during curing and exotherm.

Although other methods are available, the water content may best be determined in polyester resins by the Karl Fisher Titration Method.¹¹

Classification. Classification is necessary in resins intended for practically any use, and reduces to a minimum the confusion of the user. ¹² Fisher Scientific Co., Pittsburgh, Pa.; and Wilkin-Johnson Co., Chicago, Ill.; Penta Engineering Company, Norwood, Mass.

7.4 ± 2.7 to determine the ratio. The specific gravity value of a resin is used as a shipment-to-shipment or batch-to-batch control, and is also useful in determining the weight per gallon for packaging, shipping, or storage purposes.

Polyester resin specific gravities vary between 1.40 and 1.15 in the uncured state, and approach 1.25 in the cured (not reinforced) state. This difference between the measured and cured specific gravities makes possible a per cent shrinkage calculation:

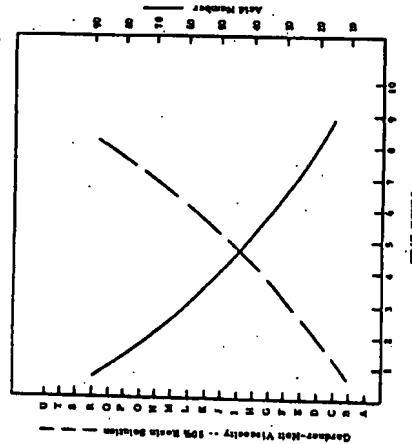


Figure II-1.2. Typical production-control curve, viscosity and acid number vs. reaction time.

the care employed in process control and also in selection of shipping containers. A classification test is desirable to indicate the presence or absence of visible foreign material or gelled particles which would be considered as contaminants. In evaluation for classification, a 25 cc portion of resin taken with a Thiele sample is diluted with 225 cc of filtered acetone. The diluted sample is then filtered through No. 4 Whatman paper on a 111 mm Buchner funnel, and the paper examined or compared with a preselected standard.

Continuously, an accelerated test at 1077 may be correlated with and used to determine approximate room-temperature stability. Almost all commercial polyesters will gel in two or three to twenty-day storage at 1077. Color. Many factors affect the color of liquid polyester, such as type and purity of raw materials, temperature and length of time of the esterification reaction, cleanliness of equipment, etc. The color of polyester resins of differing compositions varies from water-clear to dark amber. For certain end-use requirements, illu-

minations which after resin color are supplied by filling a clean, dry 20 mm I.D. x 125 mm test tube with resin, stoppering and examining in or against a north light for the presence of gelled particles or foreign substances. An arbitrary standard for type or amount of permissible foreign material may be agreed upon by supplier and user.

Storage Stability. Periods of from only three weeks to as much as twelve months are guaranteed as storage stability for various types of polyester resins, six months being specified as

times added by either the manufacturer or the fabricator. Molding temperatures, extruding index when the resin is mixed with additional monomer, and from curing and shrinkage (density change), which in turn are affected by catalyst systems and temperature. Also, aging of color of the original resin for the purpose of uniformity. In the lighter or darker resin intended for applications where decorative considerations or high light transmission are factors, color control of the resin becomes even more important.

The Gardner-Riddle viscosity comparative standards are generally employed as an index process control for polymers. The final resin color properties being judged by A.P.E.A. standards. Table II-13 presents brief descriptive comparison of these two with other methods applicable in evaluating color of liquid polymer resins.

Index of Refraction. Refractive index is defined as the ratio of the speed of light in a vacuum to its speed in the substance considered. It has some relationship to polymers to the possibility of matching the index of refraction of the transparent or translucent materials. A perfectly transparent laminate has not yet been marketed commercially, however.

resin (N_d) is less soluble in polyester than carbon dioxide; therefore, there is more likelihood of entrained gas in the resin if carbon dioxide has been used in production as the inert-gas blanket.

Tests on Liquid-catalyzed Resins

Gel-time Tests. Several tests, both principally around the "gel time" of a polyester resin, are employed to define its mechanical or physical behavior in the ultimate molding or forming operation, and, in addition, its storage stability, tank life, or gel-time drift.

Actually, the mechanism or physical changes by which polyester resins gel and cure is related to three separate phases, all related to and varying with the reactivity of the resin, the inhibitor, the catalyst used, and the curing temperature. Gelation is defined by the point at which the resin, after being catalyzed, ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. In layup or press molding, flow ceases after gelation, and no further changes may be made in any aspect of molding the product. Basically, there is an intermediate stage in which the gel thickness or becomes slightly harder, and the temperature increases slightly, whatever the temperature range in which the molding is being carried out.

Finally, a strong exotherm occurs, brought on by the full result of the chemical action of polymerization. This accounts for the curing in some types of molding, and adds to it in other types. Although polyester moldings and laminates are "wet" and for the most part usable when reduced to room temperature following the exothermic reaction, ethoxide properties are not always immediately developed, and in many cases a postcure is desirable.

Several different but related methods of defining gel time, or of using gel time to describe differences in various types of polyester, or to compare similar types, have been known and are in general usage. Due to their similarity, an attempt has been made to tabulate these methods in Table II-13. A more detailed discussion of gelation and exotherm is included under "Catalyst" in this chapter.

While the gel-time methods presented in Table II-13 give the optimum or usual requirements for the processes briefly referred to, it should be realized that variation in conditions and amounts of catalyst can greatly vary the resultant gel time. Hence, gel-time

measurement is a manufacturing tool as well as a material control. Practical experience has shown the advantage of conducting gel-time tests at the temperatures employed in manufacturing or fabricating, as well as at 120° or 180°F, if the two temperatures are different.

Air Inhibition. The surface properties of a polyester resin immediately following gel and exotherm may be evaluated by first spreading a resin film on a glass plate using a film applicator (define thickness of film to 0.010 in. or 0.020 in.), allowing it to cure at room or elevated temperature as required, and testing the surface for tack or adhesion with thin tissue paper or a probe. All polyesters are naturally inhibited by contact with the atmosphere during cure, due partially to styrene volatilization. Some compositions react less than others. For resins which must cure in contact with air (hand lay-up, spray-up), there is added, either in the thinning kettle or as-cured, an ingredient that migrates to the surface during cure and forms a thin film which actually prevents contact of the resin material with air.

Tests on Cured Solid Resins

Mechanical Properties. The mechanical and electrical properties of laminated, reinforced polyester (and other) resins are of prime importance in actually describing end-use performance, and are fully discussed in Section VIII. However, the properties of cast polyesters (unfilled and unfabricated) are useful not only in evaluating the type of resin (rigid, resilient, or plastic) but also in the control of properties. This is true because several properties of cast resins, although not as high in ultimate values as a fiber glass-reinforced laminate made from the resin in question, show greater deviation or fluctuation from specific values due to composition changes or cure variations. For this reason, cast resin properties can be used as a means of control, as well as fulfilling their specific function.

Table II-14 presents a comparison of mechanical properties of three representative polyester resins (H64, resilient, and flexible) in the cast, unfilled, unfabricated state, with a typical cloth laminate made using the rigid resin. The 12-97, 181-876, glass-treated cloth laminate will be considered a standard laminate for comparison purposes, and will be used elsewhere in this book.

The only test not referred to previously or not

TABLE II-13 COMPARISON OF SYSTEMS FOR COLOR EVALUATION OF LIQUID POLYESTER RESINS

System	Range for Polymer	Resins in this system	Remarks
Gardner-Riddle	1-5 Light to dark amber	For control during esterification process	Use viscosity sample in bubble tube. Evaluate by matching color value (ASTM-D1544).
A.P.E.A. (Glass)	0-200 (Light to dark)	Finished resin control (with or without filler or additive)	Use long-form Reader tubes. Evaluate against platinum-cobalt solution standards for color intensity (ASTM-D155).
Spectral transmission	0-100% at specific wave length	For special property measurements or comparisons	Use spectrophotometer. Evaluate against high degree of certainty which is not in all cases practical for control and processing specifications (A.O.C.S. method C-19-40).
Levichovskii, et al.	Red-60.0 Yellow-100.0 Blue-0.20	Provides separation of gray and green tints in polymers by using the red and yellow tinted glasses. The gray and green tints are not resolved using the Gardner system.	Use color-reading apparatus described in A.O.C.S. official method C-19-40.

TABLE II-14. TYPICAL MECHANICAL PROPERTIES OF REPRESENTATIVE UNSILLED, UNSUPPORTED POLYESTER CASTINGS COMPARED TO PROPERTIES OF A REPRESENTATIVE FIBER GLASS-REINFORCED LAMINATE*

	Case No.	Case No.	Case No.	Case No.	ASTM Test No.
Tensile strength, psi	16,700	16,000	*	58,700	D7900
Initial modulus of elasticity,	0.69	0.40	*	2.0	D7900
Pull strength	10,500	7,000	1,850	46,000	D683, D683
Elongation at break, %	1.8	8	65	2	D683
Modulus of rupture, psi/in.	22,000	20,700	5	20,400	D683
Impact strength, Ft./in.	0.4	0.6	1.5	25	D750
Notch, load					
Water absorption, 24 hr., %	0.21	0.23	0.40	0.13	D570
Deflection temperature under load (264 psi), °F	194	140		207	D648
Specific gravity	1.28 (Liquid 1.12)	(Liquid 1.12)	(Liquid 1.11)	(Liquid 1.40)	D792
Thermal expansion, 10°-77°	2.5	(1.42) = 1.14	(1.05)	0.8	D686
(Range D-1577)					
Hardness, Barcol	48	31	—	60	—
Units contract	100	100	25	25	—
Units tension	¼ in.	¼ in.	¼ in.	¼ in.	—

THE UNIVERSITY OF CHICAGO

Included in ASTM designations is an impression type hardness gauge test. (See footnote, Table II-14.)

RESIN CHEMISTRY

Active Ingredients

The resins commonly referred to as unsaturated polyesters are mixtures of the true ester (long-chain polymer) which results from the *condensation reaction* dissolved in a polyunsaturatable monomer which provides cross-linking units to unite the chains three-dimensionally. The two components react or copolymerize upon introduction of a peroxide (or equivalent type) catalyst to form a hard infusible thermoset.

The terminology, "unsaturated," indicates that unsaturated double bonds are carried over from the original (seed) ingredients into the finished resin to provide points of reactivity; the double bonds (unsaturations) are opened up by the free-radical catalyst and unite with similar reactive chemical groups or units of the monomer. The final curing reaction is termed as "addition" polymerization because no by-product results, as opposed to phenolics (condensation polymerization).

Other resin types similar to unsaturated polyesters are briefly described, with the main differences shown:

Allyl Reacts. These resins are composed of original reaction ingredients similar to those of the unsaturated polyesters, but are modified with fatty acid oil types (linseed, soy-*etc.*) to insure of nonoxenness. No catalyst is added, but curing is accomplished by air-drying or baking in which oxygen provides the cross-linking medium; thus the reaction is still a type of addition polymerization. The principal application of allyls is in coatings and paint.

Some resins termed allyls, but falling into the "unsaturated polyester" class, are monomerized and have had catalyst added. These are usually available as high-pressure molding compounds, ready-mixed with filler and reinforcements.

Saturated Polyesters. These are feasible resins in which none of the original ingredients are unsaturated, no monomer or catalyst is required, and the resultant linear (uncross-linked or non-three-dimensional) polyester is formed directly from the original melt into the product (fibers or film) and becomes a finished resin as it reaches room temperature.

TABLE D-1.3. RENTALS FOR DETERMINING DEL TORS

[illegible]

Foam Polyesters. These do not need on saturation, but require excess hydroxyl groups for crosslinking with a diisocyanate monomer (usually toluene diisocyanate). They also require different catalysts (amines). A liquid that is easily volatized by a slight increase above room temperature is usually added as a blowing agent. An equally effective but more costly method of inducing foaming is by inclusion of excess carbonyl groups, which function both by crosslinking and by evolving carbon dioxide during gelation. Water, turning to steam, has also been used as a blowing agent together with CO₂ from the diisocyanate. Polyester resins are preferred for flexible foams.

Unsaturated polyesters are of major interest as reinforcement plastics due to the wide variety of climates and properties which may be obtained by varying the many potentially variable new materials. These new materials fall into four classes:

(1) **Unsaturated polybasic acids** are so termed because of the doubly bonded pairs of carbon atoms included in the aliphatic molecular structure, which contains two or more carbonyl (COOH) radicals. These introduce high reactivity and rigidity into the cross-linked polyester by providing the unsaturated double bonds. Anhydrides contain one less molecule of water than the straight acids, e.g., maleic acid.

(2) **Saturated aromatic polybasic acids**, when included as a polyester resin ingredient, modify to some extent the rigidity introduced by the unsaturated polybasic acids. As with styrene, the unsaturation contained within the benzene ring structure does not enter into polymerization. There is no unsaturation outside the ring, the carbonyl groups being held by a single bond. These materials behave like saturated acids, but do not provide complete flexibility because of their rigid ring structure which is unlike the loose aliphatic structure of the saturated acids, e.g., phthalic and isophthalic acids.

(3) **Saturated aliphatic acids**, in which carbonyl groups are in an aliphatic structure, but in which no unsaturation exists, are used to modify the resin reactivity by introducing longer chain lengths between the crosslinking functions, resulting generally in the more resilient or flexible, higher molecular weight resins, e.g., adipic acid.

(4) **Polyhydric diols** (polyols), so termed because two or more hydroxyl (OH) groups exist

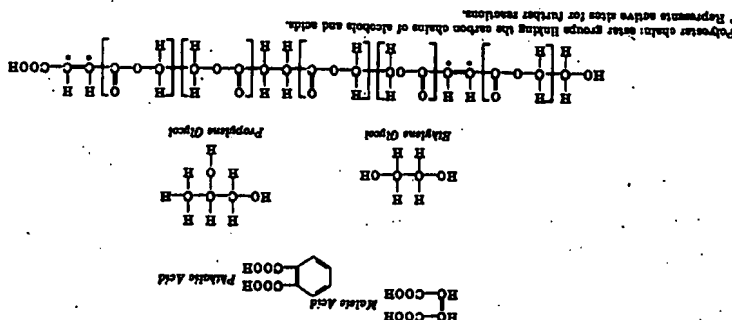
on each aliphatic glycol chain, react with either type of dibasic acid to form the ester groups. Many glycols are usable for polyester synthesis, and properties imparted are varied, ranging from rigidity to mellowness through water and heat sensitivity, e.g., ethylene glycol.

In formulating for the esterification reaction, one equivalent of acid requires one equivalent of glycol for complete esterification. A small excess (5 to 20%) of glycol is often used to bring the acid number down to a low value before polymerization has proceeded too far. The amount of water formed corresponds to the number of equivalents involved in the esterification. For each acid equivalent, one mole (18 grams) of water is formed. In the case of the acid anhydrides, only one-half mole of water is formed per acid anhydride equivalent (or, one mole per molecule of anhydride).

Hence, the organic reaction between acid and alcohol contrasts with the inorganic acid-base reaction in that the ester produced is vastly different from the secondary inorganic salt. The ester actually forms a polymer via a chemical growth process in which many single molecular units join to form a large, long-chain macromolecule, which is further added to and copolymerized by monomers and catalyst upon curing. The finished resin remains a single, low molecular-weight entity.

The fundamental dibasic acid (5) plus ethylene alcohol (6) to form the polyester resin (7) may be represented by the chemical equation 25. The esterification of polyesters is a reaction greatly aided by development of the concept of "functionality." Functionality of polymeric molecules is expressed as the number of reactive points in a molecule that function in tying it to some other molecule. Ideally, if the functionalities of either of two or more reacting molecules is only 1, no polymer will be formed. If the functionality of both molecules is 2, a thermoplastic will result; if one reacting molecule has a functionality of 3 or more and the other has a functionality of 2 or more, a cross-linked thermoset polymer can result.

The inclusion of molecular weight in any discussion of polyesters is important. Average molecular weight of the esterified polyester (before monomer addition and final cure) ranges in value from 800 to 5000. Varying the relationship of the acid and alcohol provides the greatest control over molecular weight. A general in-



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DESIGN CATALYSTS PROMOTED

TIME 11-17. ADJUSTABLE RESPONSES	Species or Strains	Particulars or Remarks
1. Methyl erythrose	1. <i>Alcaly erythrose</i>	Imparts high stability to the medium. Stimulates growth of lactinates strongly.
2. Ethyl erythrose	2. <i>Ethyl erythrose</i>	Stimulates growth of lactinates with optimum results only in systems prepared with this compound preferred.
3. Allyl methacrylate	3. <i>Allyl methacrylate</i>	More reactive than methacrylate than glycerol.
4. Acrylonitrile	4. <i>Acrylonitrile</i>	Reacts very poorly with lactinates.
5. Vinyl acetate	5. <i>Vinyl acetate</i>	Reacts very poorly with lactinates.
6. Vinyl phenol	6. <i>Vinyl phenol</i>	Reacts very poorly with lactinates.
7. Methyl methacrylate	7. <i>Methyl methacrylate</i>	Reacts very poorly with lactinates.
8. <i>N</i> -Vinyl pyrrolidone	8. <i>N</i> -Vinyl pyrrolidone	Reacts very poorly with lactinates.
9. Methyl methacrylate	9. <i>Methyl methacrylate</i>	Reacts very poorly with lactinates.
10. Methyl methacrylate	10. <i>Methyl methacrylate</i>	Reacts very poorly with lactinates.
11. Allyl diglycidyl ether	11. <i>Allyl diglycidyl ether</i>	Reacts very poorly with lactinates.
12. Methyl phenyl phosphonate	12. <i>Methyl phenyl phosphonate</i>	Reacts very poorly with lactinates.
13. Methyl carbamate	13. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
14. Methyl carbamate	14. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
15. Methyl carbamate	15. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
16. Methyl carbamate	16. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
17. Methyl carbamate	17. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
18. Methyl carbamate	18. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
19. Methyl carbamate	19. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
20. Methyl carbamate	20. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
21. Methyl carbamate	21. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
22. Methyl carbamate	22. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
23. Methyl carbamate	23. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
24. Methyl carbamate	24. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
25. Methyl carbamate	25. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
26. Methyl carbamate	26. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
27. Methyl carbamate	27. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
28. Methyl carbamate	28. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
29. Methyl carbamate	29. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.
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78. Methyl carbamate	78. <i>Methyl carbamate</i>	Reacts very poorly with lactinates.

Bekanntmachung

to prevent homopolymerization in storage. Some of the less reactive monomers do not require inhibition.

The actual mechanism of inhibition is not completely clear, but strong evidences and analytical procedures have made possible verification of theories and eventual categorizing of inhibitors into the following groups:

stopping and the following groups:

Radical inhibitors are those which, due to their ability to scavenge free radicals, result in a decomposition or reaction with free radicals from catalysts, or reaction with active polymer chain centers, prevent polymerization. These growth centers, prevent polymerization by using them as end, after which polymerization proceeds normally. "The stronger the inhibition, the more effective under conditions of stabilizing inhibitors are effective under such storage and polymerization conditions, and the longer the shelf life of the polymer." It is recommended prior to stabilizing may be necessary to remove to establish the desired cure rate. The second and preferred type are such that their action is terminated or stopped by heat, by oxygen, or by other conditions which actually cause polymerization.

Retarders are a class of inhibitors which apparently slow polymerization inception or initiation, as do the stabilizers, but the retarders interfere permanently with subsequent chain growth, or completion of the normal polymerization.

Table II-13 summarizes functions of both the inhibiting and retarding types of inhibitors as given in the literature, and also lists inhibitors used for monomers, which differ from those used for the complete polymers.

Inhibitors may be removed by washing, distillation, or filtration. The inhibitor, originally included in the monomer is usually allowed to remain, and should not be of the type to seriously interfere with polymerization.

Inhibitors are effective in concentrations as low as 0.005 to 0.15% by weight. Solutions may be prepared using approximately 5% inhibitor solids in solvents, specifically, in a 50-50 mixture of styrene and monomethyl ether of ethylene glycol.

The effectiveness of an inhibitor in a polymer may be determined by room- or elevated-temperature viscosity measurements at three-hour intervals over an extended period. That method would comprise the Brookfield viscometer, bubble tubes, and also observation of microscopical changes of bubble rise in a 13-in. tube.¹ Evaluated methods gel-time tests (GPT standard method) are also employed.

Catalysis and Curing

Table II-19 illustrates the wide ranges of operating temperatures plus typical coordinated catalyst-cromoter systems available for use with

TABLE 11-12. Investments

A. Stabilizing inhibitors		Purpose and/or Remarks
1. Oxygen		Large amounts combine with monomer for active free polymer groups and inhibit, but can be overcome by adding a reducing agent as a material that surface-etches during cure. Small amounts of O_2 accelerate polymerization by formation of peroxide; O_2 also acts as monomer probably by ultimately forming a polymer containing oxygen
2. Quinones		Probably the best and most effective inhibitor. Quinone acts immediately in solution to prevent polymerization. Quinones are not oxidizing inhibitors except in the presence of light
3. Hydroquinones		Strong inhibitors of free-radical polymerization. Quinone derivatives are good inhibitors for oxidation effect with heat (100-175°C) and extractions; require higher concentrations and inhibition effect. Better than quinone for long-term unstabilized stability, but is probably actually slowly oxidized to quinone
4. <i>p</i> -Acetyl catechol		Strong inhibitor in catalyzed polyester; some so probably actually oxidized to quinone
5. Etharietary butyl hydroquinones (2,5)		Effective inhibitor for autooxidation reaction, also for monomers, particularly acryls
6. Copper and copper salts		General polymerization inhibitor; larger quantities of Cu (and other) metal powder permit faster relatively rapid cure in presence of peroxide catalysts
7. Aromatic		Some aromatic amines act as polymerization inhibitors due to abnormal reactivity (donors) but may be cleaned and purified to eliminate inhibitory effect
8. Chalk		General polymerization inhibitor
9. Ground glass		General polymerization inhibitor
10. Silicates (organic and inorganic)		General polymerization inhibitor
11. Carbon		General polymerization inhibitor
12. Oxides		General polymerization inhibitor
13. <i>p</i> -Benzonitriles		General polymerization inhibitor
14. <i>p</i> -Nitrobenzophenones		General polymerization inhibitor
15. Phosphoroxanes		General polymerization inhibitor
16. Disulfoxanes		General polymerization inhibitor
17. Trisulfonates		General polymerization inhibitor
18. Peroxides		General polymerization inhibitor
19. Peroxide		General polymerization inhibitor
20. Phenyl <i>o</i> -naphthylamines		General polymerization inhibitor
21. Pyridine		General polymerization inhibitor
22. Phenyl hydrazine hydrochloride		Stabilizes well at room temperature and permits fast high-temperature cure
23. Triethyl benzyl ammonium chloride		Prevents cracking and discoloration
24. Triethyl benzyl ammonium chloride		General polymerization inhibitor
25. Triethyl benzyl ammonium chloride		General polymerization inhibitor
26. Triethyl benzyl ammonium chloride		General polymerization inhibitor
27. Triethyl benzyl ammonium chloride		General polymerization inhibitor
28. Triethyl benzyl ammonium chloride		General polymerization inhibitor
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96. Triethyl benzyl ammonium chloride		General polymerization inhibitor
97. Triethyl benzyl ammonium chloride		General polymerization inhibitor
98. Triethyl benzyl ammonium chloride		General polymerization inhibitor
99. Triethyl benzyl ammonium chloride		General polymerization inhibitor
100. Triethyl benzyl ammonium chloride		General polymerization inhibitor

21

TABLE 11-15—Continued	
A. Stabilizing inhibitors	Percent water sorption
13. Phenyl trimethyl ammonium chloride	Normal inhibitor
14. Trimethyl benzyl ammonium chloride	Weak inhibitor
15. Trimethyl benzyl ammonium hydroxide	Weak inhibitor
16. Alpha caproic acid	Strong inhibitor
17. Di- <i>tert</i> -octyl pyrophosphorylene diamine	Superiorly permits retention of RPO catalyst in prior to shipment (limited stability, low- er wet)
18. Para-cyclopentanes	Same as 10
1. Para- <i>tert</i> -butylphenols	Same as 10
2. Octonols diols	Same as 10
3. Tyrosinamines	Same as 10
4. Tyrosinamines	Same as 10
5. 2,4-Di- <i>tert</i> -butylphenols	Same as 10
6. 2,4-Di- <i>tert</i> -butylphenols	Same as 10
7. Tyrosinamines monoximes	Same as 10
8. Tyrosinamines monoximes	Same as 10
9. Tyrosinamines monoximes	Same as 10
10. Tyrosinamines monoximes	Same as 10
11. Tyrosinamines monoximes	Same as 10
12. Tyrosinamines monoximes	Same as 10

2. Phenylene diamine
3. Mono-4-aryldiazotopyrrolones¹⁰
4. 2, 4, 6-Tri-4-aryldiazotopyrrolones
5. 2, 4, 6-Tri-4-aryldiazotopyrrolones
6. 2, 4, 6-Tri-4-aryldiazotopyrrolones
7. 2, 4, 6-Tri-4-aryldiazotopyrrolones
8. 2, 4, 6-Tri-4-aryldiazotopyrrolones
9. 2, 4, 6-Tri-4-aryldiazotopyrrolones
10. 2, 4, 6-Tri-4-aryldiazotopyrrolones

2. 2,6-Di-*n*-butyl hydroquinone
1. p-Benzothioquinone

Has tendency with a minimum effect on oil color. No effect on stability. Particularly useful in resins intended for use at elevated temperatures.

Only slight effect on cured properties

Good stabilizer for hot-curing resins plus styrene, but has objectionable effect on resin cure, as does hydroquinone; especially in room-temperature cures. Good inhibitor for storage of unstabilized resins. Also for unstabilized resins for storage at room and elevated temperatures

Gives initial activation (*i.e.*, viscosity increases)

2. 2,6-Diethyl-p-t-butylhydroquinone

effect for times 10–15 days in polyester stored at 100°C. The results of the study of the influence of curing time on the curing of the resin with unsaturated resin catalysts are shown in Table II. The results probably be expected and should be considered in establishing resin specifications. This material is an excellent stabilizer at high temperatures, as for hot-molding resin with styrene, and also has minimum effect on subsequent resin cure. It is especially more satisfactory for use in room-temperature curing in concentrations 0.01 to 0.05%.

Stress provides a high-temperature stabilizer

TABLE II-19. Representative Tensile and Curing Systems Based on Polyurethane Resins

Type of Cure	Typical Catalyst/Promoter System	Designation of Typical Polymer
1. Delayed or B-Stage; Enhancement: activated by resin with extended catalyzed stability (with usually contains DAP monomer), cured at 23-30°C, 24-40 min.	1% benzoyl peroxide	Prepreg
2. Room temperature-cured cure (12-24 hr)	1% methyl ethyl ketone peroxide plus 0.05% cobalt naphthenate (or less)	Thick coatings
3. Room temperature-rapid cure (20 min-2 hr)	0.4 to 1.5% MEK peroxide plus 0.1 to 0.5% cobalt naphthenate or 1% BPO plus 0.25 to 0.1% di-methyl salicylate	Hand lay-up or spray-up
4. Autocurable cure (less)	0.25% BPO plus 0.5-1.5% amine hydroperoxide plus 0.25% amine promoter	Architectural sheet
5. High-temperature cure (press) Time-10 to 30 min Temperature-125 to 200°C Pressure at higher temperatures when required.	0.5 to 1.5% BPO or 1% tert-butyl hydroperoxide or 1% tert-butyl peroxide	Machined die and part and performance and cure; laminate

What means are available for generally triggering addition polymerization? There are four: thermal or photochemical means, for which no chemical catalyst is required; and either free-radical or ionic means, which involve catalysts. Free radicals are essentially responsible for polyester polymerization, and these are most generally applied from decomposition by heating, or action of a promoter on an organic peroxide. The peroxides are referred to as esters, but are not so in the truest sense, because they are consumed in the polymerization reaction. There is evidence that residual portions of free radicals exist in the network of the final product.

Assuming that a dihydric acid-dihydric alcohol monomer polyester is activated with an organic peroxide, the following mechanism is set in motion:

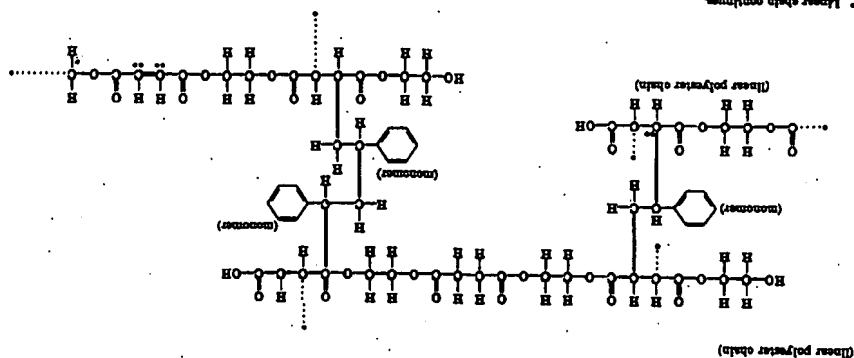
- The organic peroxide, represented as $R-O-O-R$, where R and R' may be an alkyl or aryl radical or hydrogen, decomposes by homolytic cleavage of the $O-O$ bond to release the $R-O$ and $R'-O$ free radicals.
- The free radicals first react with the chemical inhibitor which has been previously added to the resin, since the inhibitor material

must be chemically dissipated before any reaction between free radicals and the $O-C$ double bond can proceed. The number of free radicals available for polymerization can be directly influenced by solvents (if present) and inhibitors, and the rate of peroxide decomposition (free radical production) must be such as to provide for the desired rate of consumption of the inhibitor, and the desired speed of polymerization.

c) Apparently, the free radicals serve to open the double bond in the polyester linear chain to set in motion that portion of the polymerization process designated as initiation. Either the opened double bonds react with the vinyl groups of the monomer, or the free radicals serve to also open (add to) these latter unsaturated $O-C$ bonds, permitting them to perform their cross-linking function, uniting the polyester chains into a three-dimensional network. There is further evidence that free radicals may also, to some degree, react with the unsaturated monomer to form various products of decomposition. The following formula represents the chain-jointing and network growth schematically (page 25):

d) The processes which are descriptive of

POLYESTER RESINS



* Active sites (unsaturated) for further reactions.

continuation of polymerization are termed "propagation" (or chain growth) and "termination." The functionality of the resin, as well as the types and concentrations of inhibitor, promoters, and catalyst determines the rate at which propagation proceeds. Also, the extent of chain growth is limited by the number of reaction sites available for cross-linking thereby creating rigid or even brittle resin. Termination of polymer growth occurs via reactions designated as depropagation, disproportionation, coupling and chain transfer. Also, high viscosity or "flopiness" increases during polymerization will cause termination.

Theoretically, the reaction of polyester should go to completion with all double bonds reacted upon by free radicals and complete cross-linking established under the most favorable conditions. However, in actual practice, as determined by laboratory analysis, the true amount of residual unsaturation (indicating low extent of residual unsaturation) has been traced in the actual curing of polyester, and may be summarized as follows:

a) As noted previously, less than 1% of the unsaturated double bonds are reacted in the pre-catalyzed resin polyester-consumer combination.

b) After catalyzing and polymer "initiation," when chain propagation has progressed so that 85 to 90% of the unsaturation has been taken up, gelation occurs. The gel hardness and initial volume shrinkage of the resin occurs as propagation proceeds, and 40 to 60% of the total conversion is converted.

c) An incomplete cure exists when a total of 80% of the unsaturation has been utilized without the development of full properties.

d) What may be considered as an optimum cure with full properties potential realized occurs when 95 to 98% of the unsaturation has been converted. Neither extra catalyst nor post-curing will convert this slight amount of remaining unreacted material, which is sometimes removable from the cured resin by solvent extraction, but may be more accurately determined by analytical methods.

The failure of all unsaturated sites to become reacted during final cure accounts for the discoloration of polyesters upon weathering and long-term aging. The unreacted double bonds eventually take up oxygen due to the action of

sunlight, etc. and peroxides are formed, creating a yellowish or amber color.

The physical and chemical changes occurring in polyesters during polymerization may be related to the types and concentrations of inhibitor, promoters, and catalyst determines the rate at which propagation proceeds. Also, the extent of chain growth is limited by the number of reaction sites available for cross-linking thereby creating rigid or even brittle resin. Termination of polymer growth occurs via reactions designated as depropagation, disproportionation, coupling and chain transfer. Also, high viscosity or "flopiness" increases during polymerization will cause termination.

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POLYESTER RESINS

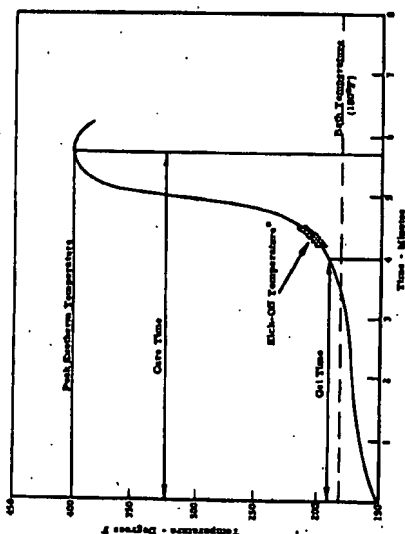


Figure 11-14. 1977 standard EPI endotherm curves for polyester resins containing 1% by volume.

Note: Peak-off temperature is not included as part of the standard EPI gel-time test.

specific resin of changes in concentration of catalyst, promoters, and fillers. Table II-11 illustrates the changes induced by catalyst content and heat-temperature variations in the standard endotherm constants of a general-purpose red-ox-type polyester (1.0 mils thick, 1.0 phthalic acid No. 45-50; 7 parts allyl to 3 parts styrene, viscosity = 13 poise).

Old time, min-sec 4-28 5-40 5-13
Cure time, min-sec 9-28 9-40 9-40
Peak exotherm °F 63 53 57

These Curves Allied Chemical Corp.

but not compatible materials (powders, plasticizers, solvents, or oils) to yield more stable solid parts, or liquid commercially usable forms. This is probably the major factor governing selection of the appropriate organic peroxide for use in initiating polymerization in polyester resins. However, ease of handling and mixing, processing temperature and time, and rate of reaction are also pertinent.

The many interesting properties found in the various peroxides are listed in Table II-12. Al-

TABLE II-10. Viscosity in Quiescent Conditions or Run, Benzene and Polymerization Resins. Standard 1977 EPI Resins. Standard Curves Test Procedures, One Part Catalyst (EPO Catalyst)

	1977	1977	1977
Old time, min-sec	4-28	5-40	5-13
Cure time, min-sec	9-28	9-40	9-40
Peak exotherm °F	63	53	57

These Curves Allied Chemical Corp.

but not compatible materials (powders, plasticizers, solvents, or oils) to yield more stable solid parts, or liquid commercially usable forms. This is probably the major factor governing selection of the appropriate organic peroxide for use in initiating polymerization in polyester resins. However, ease of handling and mixing, processing temperature and time, and rate of reaction are also pertinent.

The many interesting properties found in the various peroxides are listed in Table II-12. Al-

TABLE II-11. EFFECT OF VARIATIONS IN CATALYST CONCENTRATION AND BATH TEMPERATURES ON THE DECOMPOSITION OF A GENERAL-PURPOSE POLYESTER

Temperature, °C	Conc. $\times 10^3$, g/l	k_d , hr ⁻¹	k_d , hr ⁻¹	k_d , hr ⁻¹
100	0.5	10.3	13.4	30
100	1.0	4.6	7.3	23
100	2.0	2.5	3.5	12
100	4.0	1.5	2.3	6.5
100	6.0	1.3	2.1	6.0
120	0.5	4.4	6.3	40
120	1.0	2.3	3.5	20
120	2.0	1.3	2.1	10

though only approximately one-half the peroxide listed are in routine commercial use as polyester curing agents, all have been evaluated for potential or comparative performance in terms of polymerization rate and the heat of polymerization given in the following discussion of the vertical column headings:

a) *Heat of polymerization*, and typical range: The available heat, a prime factor, and concentration plus typical diluents are indicated.

b) *Half-life data*: In order to establish a basis of peroxide activity, the chemical kinetics were studied (Dachauer and Maggs) for decomposition of one-half the amount of a low (0.1 or 0.3 g-moles of peroxide group per liter) concentration of each peroxide in benzene through a temperature range (120–150°C) corresponding to end-use polyester processing. The thermal decomposition of peroxides in solvents is not a free-radical attack but has been shown to follow first-order kinetics. It is actually meaningless to refer to the time necessary for 100% of a material such as an organic peroxide to decompose, because theoretically, an infinite time is required. Therefore, half-life becomes a convenient parameter of peroxide activity.

Based on the residual peroxide concentration after specific test intervals at various temperatures, and applying first-order reaction rate calculations, the half-life ($t_{1/2}$) was in turn calculated from

$$k_d = \frac{0.693}{t_{1/2}}$$

where k_d is the first-order rate constant. Following the log k_d was plotted against $1/T$ (T = absolute temperature) and showed essentially straight-line relationships for almost all the peroxides tested. Reference times of one minute, 10 hours, and 100 hours were then selected, after which the temperatures required for decomposition of one-half of the peroxide at those intervals were selected from the curves and tabulated. These half-life data are reproduced in Table II-11.

Each peroxide can thus be evaluated for the order of peroxide or free-radical activity in terms of a large number of other peroxides. Also, since the original data curves can be extrapolated, it is possible to estimate the half-life of a peroxide at temperatures where it was impractical to make experimental determinations. As an example, half-lives for benzoyl peroxide were determined between 100 and 215°C, but the curve was further extended to provide data from which the following complete range of temperatures versus times for half-life decomposition was determined: 150°–100 hours; 105°–10 hours; 100°–1 hour; 95°–0.1 hour; 90°–0.01 hour. From the data it is also noted that 2,4-dichlorobenzoyl peroxide (No. 3) is the most reactive peroxide, and would be expected to initiate reactions at the lowest temperature, while 3,5-dimethyl benzoyl peroxide (No. 14) would require the highest operating temperatures to perform effectively.

c) *Activation energies* (ΔE) were calculated in the same way for all the peroxides which showed first-order decomposition. The activation energy may be determined from measurements of the specific rate constant (k_d) at two or more temperatures according to the following equation or by plotting $\log k_d$ against the reciprocal of the absolute temperatures ($1/T$), the slope of the resulting straight line being equal to $\Delta E/2.303R$:

$$\log \frac{k_2}{k_1} = \frac{\Delta E}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where R = the universal gas constant (1.987 cal deg⁻¹ mole⁻¹).

Since for first-order decomposition (formula 9 for k_d applies), ΔE can be calculated from the slope of the line obtained by plotting $\log k_d$ versus $1/T$. The degree of slope of these lines is

a direct qualitative measure of the activation energy associated with each peroxide.

From a practical standpoint, peroxides with high activation energies will decompose over a narrower temperature range or provide a larger number of free radicals in a given temperature range, than those with low activation energies. Hence, if an initiator is required that will show a narrow decomposition range, a high activation energy is desired. If a slow, steady decomposition is required, a low activation energy would fill the need.

Although both relative peroxide activity and activation energy can be reliably changed by the introduction of a radical scavenger, the latter function in the half-life and activation energy studies may be considered as basic data necessary for the choice of an effective initiator for any free-radical polymerization system.

d) *Half-life temperature*: In Table II-11, it was noted that the half-life temperatures were depressed with increased catalyst concentration, and that gel and cure times correspondingly shortened. Also, as specified, the half-life temperatures remained constant during changes in the bath temperature used as a reference point for the temperature curve determination. The half-life temperatures in Table II-11 are dependent in that, by operating at or above the half-life temperature range for a particular initiator system, rapid cure can be obtained.

e) *Oil Time Data*: Standard SFT gel time determinations for 1% of the commercial form of each peroxide listed were made in a 150°C bath (unless otherwise noted) using the reference polyester (formulas on page 37). These data are indicated for purposes of coordinating gel times with half-life data and half-life temperatures to further assay peroxide activity.

Determination of a reliable mathematical relationship between the rate of formation of active free radicals in a given peroxide and the gelation time of a normal concentrated polyester would be difficult because of the many variables involved. However, a ten-hour half-life for many of the peroxides studied corresponded very nearly to the temperature at which a 15-minute gel time was obtained.

f) *Effect of Mixed Catalyst Systems*: Experimental curves were run at 150, 115, 100°C. Total peroxide concentrations comprising an active catalyst, will develop optimum properties at a slow rate after gelation and cure. In the early days of hand lay-up usage, eight hours' total mold time was required to produce a large item such

natural and inhibitory effects were noted. The synergistic or catalytic effect of the peroxide combination and the then which showed inhibition are listed at the bottom of the tabulation, with a reference made by number.

g) *Function and Structure*: These organic peroxides employed as catalysts in commercial polyester practice are so indicated, and the temperature range in which they have been found to be most useful is also classified. The functions of the organic peroxides when used as initiators for polymerization systems other than those for polyester are briefly referred to.

In addition to those peroxides cited in Table II-11, it has recently been brought to light that certain types of epoxy-resin hardeners (epoxy resin plus a hardener) function as polyester polymerization initiators when used with or without peroxide catalyst. The epoxides themselves do not initiate free-radical polymerization, but undergo a free-radical reaction at the carbon group.

Promoters

Figure II-12 has been prepared to provide an illustration of the effect of two members of a specific group of chemicals, termed "promoters," in accelerating decomposition of peroxide catalysts interdispersed with polyester resin at temperatures below the normal decomposition and activation temperatures of the particular peroxide.

For methyl ethyl ketone peroxide, a half-life of 15 minutes at 100°C is exhibited, and gelation occurs in approximately 15 hours in a standard polyester resin at room temperature for a concentration of 1%. Curve A compares how the temperature gel time may be shortened to 80 minutes by the incorporation of 0.5% of the promoter, which implements (the catalyst itself), and further decreased to 10 minutes by additionally increasing 0.1 per cent dimethyl sulfoxide (Curve B), termed the secondary promoter. Note the particular effect of the latter cure (by DMA) in raising the peak exotherm temperature.

It is fairly well-known that a simple one-promoter system such as cobalt naphthenate, used together with methyl ethyl ketone peroxide, will develop optimum properties at a slow rate after gelation and cure. In the early days of hand lay-up usage, eight hours' total mold time was required to produce a large item such

[illegible]

TABLE II-13. PROPERTIES OF ORGANIC FLUORIDES

[illegible]

RESIN CATALYSTS, PROMOTERS

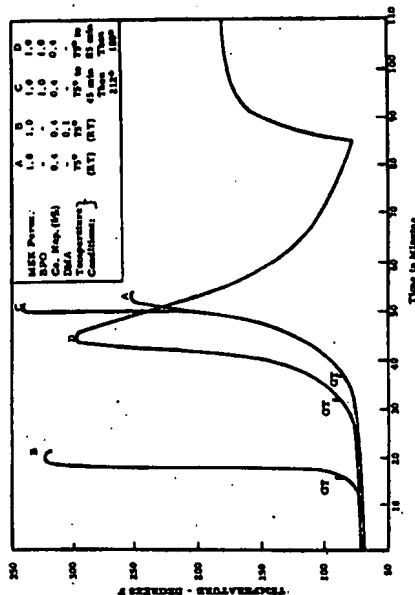


Figure 11-15. Isotherm curves for room-temperature curing systems in polyester resins.

as a heat. By using a double-panned system, through the cure cycle, no secondary condensation results if the resin is subjected to an elevated temperature (as for postcure). In actual practice, the degree of cure may be considerably advanced by postcuring at elevated temperatures. In addition to making DSC gel-time test measurements, advancement of a cure prior to gelation may be observed by noting the viscosity increase of the resin. Following gelation, operation of the resin is possible. Several gauge readings make possible a graphic or numerical tracing of the cure. After a laminate has been formed, condensation or noncondensation of a complete cure may be determined by (a) measuring per cent retention of ultimate flexural strength after a two-hour boil in distilled water, and also by (b) making certain that no increase in flexural modulus is observed. Additional heat making certain that no increase in flexural modulus of elasticity greater than 15% results when the laminate is subjected to a postcure of two hours at 180°F. In the two-hour boil test, insufficient original cure is indicated by wet values in excess of the dry values, since heat from the boiling water advances the resin cure beyond its expanded state.

As previously indicated, promoters are also used for specific applications at intermediate and

Resin	Catalyst	Promoter	Temp. (°F)	Time (min)	Notes
1. 1,4-Bis(hydroxymethyl)benzene (BPA)	1. 1,4-Bis(hydroxymethyl)benzene (BPA)	1. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	1. 1,4-Bis(hydroxymethyl)benzene (BPA)
2. 1,4-Bis(hydroxymethyl)benzene (BPA)	2. 1,4-Bis(hydroxymethyl)benzene (BPA)	2. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	2. 1,4-Bis(hydroxymethyl)benzene (BPA)
3. 1,4-Bis(hydroxymethyl)benzene (BPA)	3. 1,4-Bis(hydroxymethyl)benzene (BPA)	3. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	3. 1,4-Bis(hydroxymethyl)benzene (BPA)
4. 1,4-Bis(hydroxymethyl)benzene (BPA)	4. 1,4-Bis(hydroxymethyl)benzene (BPA)	4. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	4. 1,4-Bis(hydroxymethyl)benzene (BPA)
5. 1,4-Bis(hydroxymethyl)benzene (BPA)	5. 1,4-Bis(hydroxymethyl)benzene (BPA)	5. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	5. 1,4-Bis(hydroxymethyl)benzene (BPA)
6. 1,4-Bis(hydroxymethyl)benzene (BPA)	6. 1,4-Bis(hydroxymethyl)benzene (BPA)	6. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	6. 1,4-Bis(hydroxymethyl)benzene (BPA)
7. 1,4-Bis(hydroxymethyl)benzene (BPA)	7. 1,4-Bis(hydroxymethyl)benzene (BPA)	7. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	7. 1,4-Bis(hydroxymethyl)benzene (BPA)
8. 1,4-Bis(hydroxymethyl)benzene (BPA)	8. 1,4-Bis(hydroxymethyl)benzene (BPA)	8. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	8. 1,4-Bis(hydroxymethyl)benzene (BPA)
9. 1,4-Bis(hydroxymethyl)benzene (BPA)	9. 1,4-Bis(hydroxymethyl)benzene (BPA)	9. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	9. 1,4-Bis(hydroxymethyl)benzene (BPA)
10. 1,4-Bis(hydroxymethyl)benzene (BPA)	10. 1,4-Bis(hydroxymethyl)benzene (BPA)	10. 1,4-Bis(hydroxymethyl)benzene (BPA)	100	10	10. 1,4-Bis(hydroxymethyl)benzene (BPA)

Table 11-15—Continued

TABLE II-1.12. COMPARATIVE EFFECTS OF COMMONLY USED PROMOTERS ON THE GEL AND CURS CHARACTERISTICS OF VARIOUS PEROXIDE CATALYSTS

[illegible]

REAGENTS, CATALYSTS, PROMOTERS

elevated temperatures; however, their main usage is in the room-temperature and intermediate-temperature cure systems. The variation in gel time be rigidly observed. The variation in gel time the explicit instructions of the manufacturers regarding catalysis and use of each resins should be rigidly observed. The variation in gel time

General characteristics to be desired in a promoter are: compatibility with, or solvency in a medium compatible with the polymer resin; low cost; lack of toxicity; and freedom from post-cure odor, discoloration, or interference with curing.

complete polymerization. Required promoter concentrations are usually determined empirically to suit specific systems, and range from 0.01 to 5.0%, with 0.05 to 0.1% optimum for the majority of promoters.

Table II-13 presents a listing of the parameters resulting from the fitting of the experimental results. The values of the rate constants for the various steps are generally in good agreement with those reported in the literature.¹⁰ The values of the activation energies for the various steps are also in good agreement with those reported in the literature.¹⁰ The values of the pre-exponential factors are also in good agreement with those reported in the literature.¹⁰ The values of the equilibrium constants for the various steps are also in good agreement with those reported in the literature.¹⁰ The values of the rate constants for the various steps are generally in good agreement with those reported in the literature.¹⁰ The values of the activation energies for the various steps are also in good agreement with those reported in the literature.¹⁰ The values of the pre-exponential factors are also in good agreement with those reported in the literature.¹⁰ The values of the equilibrium constants for the various steps are also in good agreement with those reported in the literature.¹⁰

Aspects from toxicity precautions, if and when called for, the cardinal rule governing use and handling of promoters is: do not use them directly with any catalyst materials outside the resin bath. Almost all promoters act as powerful reducing agents and induce explosive reactions when placed in direct contact with peroxide catalyst materials.

APPLICATIONS

There are five major classifications of methods of processing Reinforced Plastic, simply listed as follows with subdivisions, and more fully described in Section IV, *Molding Methods*.

A. as an easy spray-on, processing and lay-up, bag making, spray-on, processing and lay-up, use of pre-preg material, contour weaving, sandwich construction, potting and encapsulation, potting, gel coats and other coatings, insulation, putties, gel coats and other coatings, non-dissolvable binder resins. Medium- to slow-speed room-temperature curing systems apply

B. Matched-Die Molding Methods, including preform molding, premix molding, and injection and transfer processes. Rapid, elevated

C. *Filament Winding Methods*, which comprise either wet or dry application of continuous filament fiber-glass reinforcement, or applica-

3

elevated temperatures; however, their main advantage is in the room-temperature and intermediate-temperature cure systems.

General characteristics to be desired in a promoter are: compatibility with, or solvency in, the material compatible with polyester resins; low cost; lack of toxicity; and freedom from post-cure odor, discoloration, or interference with complete polymerization. Required promoter concentrations are usually determined empirically to suit specific systems, and range from 0.01 to 5.0%, with 0.05 to 0.1% optimum for the majority of promoters.

Table II-13 presents a listing of the comparative reactivity of seven of the more commonly used promoters, and (for comparison) of an inhibitor, all at 0.5% concentration in each of eight specific peroxide catalysts.¹⁰ In reporting the data of Noller, Stangel, and Magelli, both temperatures in which the emulsion curves were run are given, as well as half-of-temperatures, gel and cure times, and peak emulsion temperatures. The bath temperatures used determine the temperatures of the emulsion.

ended upon the type of parasite and the additive being tested, and was also selected so as to show an infection in the isotherm curve from which the kick-off temperature could be determined. In the instances where reported kick-off temperatures are below 180°F, the "kick-off" occurred before the sample reached bath temperature.

The basic unsaturated polyester used for all determinations was composed of 1.0 maleic anhydride, 1.0 phthalic anhydride, 2.3 propylene glycol, hydroquinone 0.013%, reacted to an acid number of 45-60, and seven parts of the reacted alkyl mixed with three parts of monomeric styrene.

A further summary of promoters cited in the literature, together with remarks indicative of their particular function or properties, is presented in Table II-14. This listing may be considered as a general reference in planning use of a promoter-catalyst system for particular curing requirements.

Promoters are usually incorporated into the system by the manufacturer to provide a balanced system with guaranteed uncatalyzed and catalyzed potencies and excellent long-term storage stability. A solution may be desirable for better dispersal. Mixing must be thorough to provide the necessary cured-state uniformity. One- and two-part systems are available. The one-part and double-promoted resins usually have shorter storage lives and are more temperature-sensitive than unpromoted resins; hence,

Don't sweat it on a B

Table II.14. Function of Various Promoters Used with Polyurethane Resins

Promoter	Promoter action Remarks
Inorganic Compounds:	
1. Butyl chloride	Effective initiator for polyurethanes but are limited in application (General).
2. Hydrogen sulfide	Same as No. 1.
3. Stannous chloride	These and other multivalent metals in a low oxidation state behave as promoters. Other ferrous and stannous salts are also applicable.
4. Ferrous chloride	Acts as inhibitor with organic peroxide alone, but acts as accelerator with peroxide plus conventional promoter.
5. Carbon black	Increases room-temperature cure rate at 10 to 20% with some conventional promoters. Similar effect with peroxide plus organic oxides and hydroxides of barium, strontium, magnesium, and also calcium oxide.
6. Calcium hydride	H ₂ O, H ₂ O ₂ are effective as room-temperature promoters, but have no primary in high-temperature cure.
7. Inorganic reducing agents	
Organic Compounds:	
8. Cobalt naphthenate, 6%	Widely used (0.1-1.0%) as room-temperature-cure promoter with methyl ethyl ketone peroxide or cyclohexanone peroxide. Room-temperature systems using cobalt naphthenate as the sole promoter do not rapidly develop optimum properties as indicated by tensile ¹⁰ and wet-tensile ¹¹ reaction tests. An accessory promoter is desirable. Cobalt itself is also supplied in another more concentrated form (Cobalt 82-24, containing a chelating agent) than cobalt naphthenate. Both forms strongly color the resin more gradually after having been incorporated into the polymer and impart some tinging to the cured part; which can usually be masked with fillers or pigments. The cobalt itself present provides the true reaction with catalyst to release free radicals. An aromatic amine widely used (0.05 to 0.5%) as an accessory room-temperature-cure promoter with cobalt naphthenate, and also as a room-temperature-cure initiator with BPO catalyst. DMA is cheap and effective for fast gel and cure, but is toxic, malodorous, and is generally not desirable in gel casts and casts exposed to be exposed to sunlight and weather due to discoloration upon aging. Concomitantly, a larger percentage content than DMA for an equivalent gel time, but provides a shorter cure time, hence produces a lower molecular-weight polymer which is not quite as strong. DEA has some advantages over DMA in producing less gel time drift on aging after the promoter is incorporated into the resin. DEA is also cheap but is toxic and will produce discoloration upon aging. Similar to performance to DMA and DEA and generally used in similar applications. This promoter discolors more slowly and to a slightly lesser degree, and is less toxic than DMA or DEA. However, it is more expensive and slightly slower or more sluggish in curing. Not commonly used.
9. Dimethyl sulfone	Used together with 1-iodoethyl mercaptan in promoting room-temperature gelation and curing using common hydroperoxide as catalyst.
10. N,N'-dimethyl sulfone	
11. N,N'-dimethyl-p-toluidine	
12. N-phenylthioamide	
13. 1,2-dithiolthione	

Table II.14.—Continued

Promoter	Promoter action Remarks
14. N or 1-iodoethyl mercaptan	Mercaptan provides a solution promoter exhibiting no discoloration on aging, and reportedly prevents air-inhibition on curing when used with common naphthenate and 1-ethyl hydroperoxide. However, they actually produce gelation but do not cure by themselves, hence must be added only at the same time as the catalyst. Since the mercaptan gel the resin, and the catalyst cures, the best cure is obtained by adding a catalyst, a promoter, and a curing agent. Mercaptan also gives a very good time results when used as promoter in concentrations of less than 0.05%. They are colorless and generally regarded as not being so effective for promoting as are the aromatic amines. Not commonly used.
15. 2,4-diphenyl p-benzoquinone and others are inhibitors at room temperature in polyester resins, but show some activation effect when stored at elevated temperatures (107°). ¹² 2,4-Di-tert-butyl hydroquinone combines good room-temperature inhibition with minimum propagation of cure at elevated temperatures. Hydroquinone derivatives are not in general use as promoters. Not commonly used.	
16. Triethylene diphenylphthalate	Onset of cure at room temperature is difficult as for cobalt naphthenate. No advantage.
17. Phosphoric acid chloride	Discolors more strongly than cobalt naphthenate. No advantage over cobalt naphthenate.
18. Hydroquinone derivatives	No advantage over cobalt naphthenate. Discolors strongly. Shortens room-temperature gel times of all peroxides except BPO and 0-1-tert-butyl peroxide. Basis of other proprietary promoters. Used at 5% in resins promoted with 1-ethyl hydroperoxide for faster cure at higher temperatures. Not commonly used.
19. Ferric acetyl acetate	Same as above. Not commonly used.
20. Magnesium naphthenate or stannous	Used 0.05 to 0.15%. More commonly used as a catalyst for the catalytic reaction of allyls. Not commonly used.
21. Stannous acetate	Not commonly used.
22. Ferric acetate	Similar to dimethyl sulfone. Not commonly used.
23. Phenyl phosphine acid	Onset of cure at room temperature is difficult in intermediate temperature cure (acidic nature); inconsistent in gel-time behavior. Not as effective as aromatic amines.
24. N-tert-butyl sulfone	Employed (0.15 to 0.5%) for fast room-temperature cure of commonly inhibited polyurethanes. Not commonly used.
25. Diphenyl hydroxyphenylphosphine	Similar to performance to, but not as effective as DMA and DEA. Not commonly used.
26. p-toluenesulfonic acid	Same as above. Not commonly used.
27. 4,4'-tetramethyl diamine di-phenylphosphine	Useful promoter but requires external heat for activation. Not commonly used.
28. N-phenylthioamide	Same as No. 12.
29. Acrylic acid and benzoinic acid	Same as No. 12.
30. Dimethyl phosphine	Used for complete cure. Not commonly used.
31. Triethanolamine	Used (0.01 to 1%) together with peroxide catalyst to obtain clarity in laminates. Not commonly used.
32. Tri-n-propylamine	Methyl iodide (0.1-1.0%) stabilizes against discoloration caused by some peroxide catalysts, but laminates hardness is somewhat diminished. Not commonly used.
33. Sodium sulfonate or diethyl mercaptan	
34. Methyl iodide	

Table II-11A—Continued

Promoter	Promotes under Remarks
40. Quaternary ammonium compounds	Most quaternary ammonium chlorides are effective promoters, but some perform as inhibitors. The promoters may be effectively incorporated into the resin with stability, but produce discoloration. Several proprietary promoters are based on these compounds.
41. Hydrogen halides	Proprietary—difficult to promoting effect to quaternary ammonium chlorides.
42. Cobalt Isonitrate	Room-temperature cure promoter with cyclohexanone peroxide or methyl ethyl ketone peroxide. The cobalt metal ions are the active promoters, hence no advantage over cobalt naphthenate.
43. Propylene diamine	Not an accurate catalyst. Not commonly used.
44. Triethylamine	Not an accurate catalyst. Not commonly used.
45. Methylene ethanediol	Similar to ethoxydiurethane. Not commonly used.
<i>Naphthenate Promoters:</i>	
46. Ultraviolet radiation ^a	Free radicals are produced in polymers by action of artificial ultraviolet radiation (2000 Å), also by exposure to sunlight. Both will promote cure in polymers emulsified with benzal (5%) or benzoin (5%). Benzoin is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 277° K. No peroxide catalyst is required, but may be used (2000 preferred). The total amount of initiator may be added into the resin with compound. Benzoin emulsified stability (in dark), promoting catalysts which are more stable than benzoin. Benzoin emulsified stability (in dark), promoting catalysts which are more stable than benzoin.

Free radicals are produced in polymers by action of artificial ultraviolet radiation (2000 Å), also by exposure to sunlight. Both will promote cure in polymers emulsified with benzal (5%) or benzoin (5%). Benzoin is more stable and provides long pot life; benzoin is more reactive and is preferred. Both provide gel times of thirty minutes after exposure starts, even at 277° K. No peroxide catalyst is required, but may be used (2000 preferred). The total amount of initiator may be added into the resin with compound. Benzoin emulsified stability (in dark), promoting catalysts which are more stable than benzoin. Benzoin emulsified stability (in dark), promoting catalysts which are more stable than benzoin.

G. Ambient humidity^a

For most relative humidity reportedly acts to affect room-temperature cures together with temperature and activator concentration variables. Water acts as a good inhibitor, but only a very small percentage can be tolerated due to its deleterious effect on cured resin properties.

TABLE II-11A VARIATION IN GEL TIME WITH TEMPERATURE AND RELATIVE HUMIDITY FOR A TYPICAL RAYON BOND-TYPE QUATERNARY AMMONIUM PROMOTER RESIN

Temperature, °F	Relative Humidity, %	Gel Time in Minutes at 277° K
60	50	15
70	50	15
80	50	15

Notes: Courtesy of Raychem Corp.

tion of prepolymer materials to a reacting form. High-temperature oven cures are employed.

D. Acceleration methods, including solid red stock, below tiling and piping, structural cross-

resistance to cracking, rigidity or resistance (affecting mechanical properties), surface gloss and hardness, are among those obtainable.

However, there are five specific classes of polyester resins which have been developed with widely divergent properties to satisfy the performance requirements of the fields in which they are called upon to serve as components of RP. These five resin types have individually received from the best-known combinations of resin ingredients (Table II-1.1), common (Table II-1.2) and curing systems to produce the desired qualities. As long as the solvent and properties of the resin are maintained, any of the mixing methods may be resorted to, and any of the handling and processing-improvement characteristics may be incorporated. The final films of resin-type performance are not functions of demerits, i.e., high heat-deflection temperatures resins may also show superior chemical durability.

Brief descriptions of the five major classes follow:

General Purpose

These multipurpose resins make possible the good electrical and mechanical properties for which polyesters are noted, augmented of course by the reinforcement. They may be either rigid or resilient, filled or colored, and are used for general, nonreinforced, decorative molding items. They also possess average-to-good chemical resistance, and, of course, may be infinitely modified to suit the great variety of molding processes and curing cycles. They will show discoloration, loss of gloss, and their blooming upon weathering, have a maximum long-term pot, continuous-exposure temperature of 257° F. Electrical resistance is good and may be further improved by incorporating diallyl phthalate monomer, but cure time and amount of catalyst required are correspondingly increased.

Light-Stable and Weather-Resistant Resins

These resins are manufactured to possess high clarity and freedom from any amber fluorescence due to processing (APFA = 20 to 100). Low viscosity (1.4-4.0 poise) for rapid wet-out of reinforcement, rigidity and high modulus for rapid cure, and also high surface gloss and hardness. They usually contain a mixture of styrene and methacrylonitrile or methacrylate-
also monomers to provide freedom from surface

erosion and fiber blooming on weathering, and also contain stabilizers to resist yellowing or darkening due to action of ultraviolet rays in sunlight (phenyl salicylate and ortho-hydroxybenzophenones derivatives are typical stabilizers).

Creation of a resin-rich surface layer provides good insurance against surface erosion and fiber blooming. Polyester gel coats prevent fiber erosion during long and continuous outdoor exposure, but are subject to cracking. Laminates made from transparent light-stable resins with standard approximately four years in a temperate climate (less in subtropical climates), prior to serious fiber blooming. The cracked laminates may be rejuvenated with applications of clear lacquers. Recent developments have made possible application of a weather-resistant film on the laminate surfaces during manufacturing; the film remains an integral part of the laminate.

While not completely transparent, the light-stable and weather-resistant resins (Duro, Lantac) may be tinted and used in house or industrial structural glazing, as interior decorative panels. These panels are strong, light in weight, shatterproof, and are enjoying acceptance and increasing annual production as an outstanding application of RP.

Chemical-Resistant Polyester Resins

Utilization of chemical-resistant polyester resins to supersede metal structures which are inordinately subject to rust and corrosion is only in its infancy. Large-scale structures (flume testing and hard by-up) predominantly (starch, duct, block, piping, etc.), but high-temperature matched-to molded problems and present parts are also in wide usage.

The main cause of chemical attack of resins in aqueous environment is hydrolysis, which results in chemical decomposition due to attack and resultant rupture of the ester linkages in the polymer chain. Chemical-resistant resins have been designed so that ester linkages replace a percentage of the ester linkages by reacting phenolic acid and a high-potential A-intermediate, and adding styrene monomers. Establishment of more of a ring structure than that found in a general-purpose polyester resin. The higher molecular weight of such a resin also contributes to the resistance to hydrolysis.

Polyester resins with increased chemical durability and thermal stability, improved strength properties, which also permit blending with

No.	Author(s)	Title or Subject	Vol.	P. no.	Year
4	Bjorkstrom, J.	SP1-B.P. Dir. Proprietary	13	1-A	1958
5	Johnson, O. B.	SP1-B.P. Dir. Proprietary	14	17-A	1959
6	Mander, A. L.	SP1-B.P. Dir. Proprietary	15	1-A	1960
7	Porter, C. F.	SP1-B.P. Dir. Proprietary	13	15-A	1957
8	Osaka, R. A.	SP1-B.P. Dir. Proprietary	11	17-C	1958
9	Loewy, J. R.	"Glass Reinforced Plastic," London, Ellis & Sons, Ltd.	—	28, 41	1957
10	Shultz, A. L.	"Polyester Resins" New York, Reinhold Publishing Corp.	—	—	1960
11	Morgan, P. A.	"Polyesters and Their Applications," New York, Reinhold Publishing Corp.	—	—	1959
12	Bjorkstrom, J. et al.	WADO Rev. of Structural Plastics	—	1	Sept., 1959
13	Nath, R. G.	"Polyester Resin Materials Study," Minnesota Chemical Co.	—	—	Jan. 19, 1959
14	Burns, R. B.	Modern Plastics	29	14	1958
15	Burns, R. B.	"Composition and Utilization of Polyesters," Allied Chemical Corp.	—	—	1954
16	Palmer, J. F. Jr.	General Electric Co.	—	—	1957
17	Osaka, R. A.	Personal Communication, Gild. Am. Co.	—	—	July 16, 1959
18	Atlas, S. M.	Intern. Ed. & Technol.	Prototype	44	1961
19	Mark, H. P.	"Polyester and Resins," Princeton, N. J., D. Van Nostrand Co.	—	33	1959
20	Golding, S.	Ind. & Eng. Chem.	46, No. 8	1519	1954
21	Burns, R. B.	Ind. & Eng. Chem.	46, No. 8	1648	1954
22	Chen, W. R.	Ind. & Eng. Chem.	46, No. 8	1648	1954
23	Bochwalter, T. E.	Ind. & Eng. Chem.	46, No. 8	1615	1954
24	Feuer, S. S.	Ind. & Eng. Chem.	46, No. 8	1615	1954
25	Essential, I.	Ind. & Eng. Chem.	46, No. 8	1615	1954
26	Sims, C. B.	Ind. & Eng. Chem.	46, No. 8	1615	1954
27	Ellis, O. M.	"Analytical Chemistry of Polymers, Part I," New York, Reinhold Publishing Corp.	15	649	1959
28	Riddle	"Monomers Acrylic Esters," New York, Reinhold Publishing Corp.	—	—	1954
29	Steen, M. C.	SP1-B.P. Dir. Proprietary	—	—	Oct., 1960
30	Ann.	Techn. Bulletin No. 3-201, Miles Chemical Co.	—	—	—

GENERIC CATALYST, PROMOTER

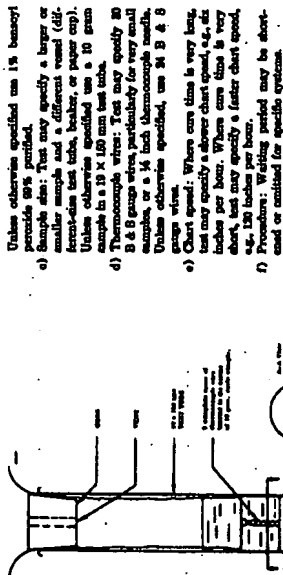


Figure 12-1: Sketch of thermocouple in test tube.

B. Report

Measure and record the following information from these curves which are considered reliable.

- Time from 1077 to bath temperature.
- Time from 1077 to 1077 above bath temperature.
- Peak temperature.

6. Variations

- Bath temperature and fluid: test may specify a different bath temperature and/or fluid (1077, room temperature, etc., etc.)
- Catalyst: test may specify a different catalyst (1077, room temperature, etc., etc.)
- Sample size: test may specify a different sample size (1077, room temperature, etc., etc.)
- Wire size: test may specify a different wire size (1077, room temperature, etc., etc.)
- Chart speed: test may specify a different chart speed (1077, room temperature, etc., etc.)

Notes: Test may specify different catalyst and/or a different catalyst concentration.

References

No.	Author(s)	Title or Subject	Vol.	P. no.	Year
1	Mitchell, J. Jr.	"Organic Chemistry," Vol. 1, New York, Interscience Publishers, Inc.	—	11	1953
2	Edwards, R. S.	Research Report No. 15, Purdue University, Lafayette, Ind.	—	—	Nov. 15, 1958
3	Lawson, O. D.	SP1-B.P. Dir. Proprietary	16	Follows in specialty	1961
4	Ann.	SP1-B.P. Dir. Proprietary	—	—	—

TABLE II-3.1. Phenolic Resin Types

Classification	Chemical Composition	Physical Properties
Condensation resins	Phenol + 1.0 to 1.5 formaldehyde + 0.5 to 1.0 water	Phenol + 1.0 to 1.5 formaldehyde + 0.5 to 1.0 water
Reaction catalyst	Strong bases, i.e., NaOH, KOH, EOH, quaternary ammonium compounds, and combinations; quantity required = 0.1 to 0.5% of phenol charge. Catalysts are usually added with the phenol.	Weak bases, i.e., NH_3 , primary, secondary, and tertiary amines; quantity required = 0.1 to 0.5% of phenol charge.
Method of handling and characteristics of the resin	Removed from reactor and cooled; maintained as a liquid.	Condensation water removed; removed from reactor and cooled; added to the powder or left in lump; resin may be redissolved if necessary.
General properties (increased data)	Water-soluble; viscosity = 100 to 1000 poise at 100°C. Sp. gr. = 1.05-1.25; solids are thermosetting.	Slightly soluble in water; viscosity = 100 to 1000 poise at 100°C. Sp. gr. = 1.05-1.25; solids are thermosetting.
Stability	Unstable; must be refrigerated prior to use to delay advance of the reaction process.	Stable; must be refrigerated prior to use to delay advance of the reaction process.
Curing requirements and behavior	Cures by heat or change of pH or both; solids catalysts may be added.	Cures by heat and low pH; added catalysts may be added; partial pre-curing is possible.
Typical use	Blends, coatings and casting.	Industrial and decorative laminates, adhesives.

Chapter II-3

PHENOL-FORMALDEHYDE RESINS

Although the reaction between phenols and formaldehyde has been known since 1872, the chemist Leo Baekeland, through the period 1900-1909, systematically combined the reactants on an organized mole basis and actually became the first to establish commercial uses for the phenol-formaldehyde resinous product.

Baekeland solved the then major problem of oxidation of resins during cure by introducing pressure molding. He also compounded the original phenolic molding compounds by adding fillers to phenolic resins to reduce their brittleness after molding. He prepacked and laid the groundwork for the present Reinforced Plastic Industry by using phenolic resins in liquid form to impregnate paper and fabric, which were dried and ultimately press-cured, making possible both industrial and decorative laminates.

Furthermore, the development of phenol-formaldehyde resin technology co-acted the expanding use of electric power in America. Because of their desirable electrical insulating properties and ease of molding, phenolics were placed in service to satisfy numerous industrial and domestic electrical requirements.

(1) Phenol-formaldehyde and catalyst are charged and the mix temperature raised to 140 to 180°C accompanied by adequate agitation. Resins remain as a continuous phase during reaction, while novolaks separate into two phases between which contact must be maintained by the agitation.

(2) Exothermic heat is generated when the reaction goes under way, and must be dissipated by refluxing under vacuum or by cooling-water coils inside the kettle.

(3) The reaction is carried to the stage at which from 50 to as much as 99% of the formaldehyde has been converted. This is determined by continually testing for free formaldehyde (see appendix to this chapter). The amount of free formaldehyde allowed to remain is governed by the contemplated end use. Viscoelasticity is also controlled by the degree of reaction and increases as polymerization progresses.

(4) Water is removed by vacuum distillation (40-60°C) from the reaction to which is to be added and from the novolaks which are to become solid resins and in which molding points must be controlled. These latter resins must be as free as possible of volatiles. Water is

PHENOL-FORMALDEHYDE RESIN MANUFACTURE

Essentially, any of the compounds classed as phenols may be reacted with any aldehyde to yield a resin of the phenol-formaldehyde type (also known as phenoplasts or phenoplasts). However, phenol ($\text{C}_6\text{H}_5\text{OH}$), also carboxylic acid, phenylsulfonic acid, or hydroxybenzenes and formaldehyde (HCHO), also oxymethylene, formalin, or formaldehyde, constitute respectively 75 and 95% of all present phenolic synthesis production. Phenol is commercially desirable because of its high purity and lower cost, and

generally permitted to remain in the storage tank, but the total amount of residual water is varied depending upon the end-use requirements.

(6) Liquid resins are cooled and pumped to storage or shipping containers. The sorbents are dropped to adduct in pans or onto a clean floor. They must be cooled rapidly to retain the melting point at the determined value, and are broken up into either pulverized, flaked, granulated, or other solid forms. To produce liquid novolac resin, reaction products are redissolved in alcohol or other solvent prior to removal from the kettle.

Note: The condensation reaction is brought to completion as possible in the kettle preceding. To prevent further advances of cross-linking prior to ultimate use, one-step phenolics must be refrigerated, but two-step phenolics will exist at room temperature. The latter are usually stored in a cool, dry place, but probably slight condensation occurs as the ultimate rigid condensation polymer is formed.

A normal phenolic batch reaction requires from four to twelve hours for completion. Processes variations consist of reacting in pressure vessels or by a continuous process, making possible greatly reduced reaction time. These variations are suitable only to specific resin types, however.

The chemistry of phenol-formaldehyde resins is described as (a) little understood and (b) as a complex combination of condensation and addition polymerizations and rearrangement of groups, all of which may occur simultaneously. Excellent surveys of these reactions have been published, nevertheless, and these may be summarized as follows:

In formation of resins, the steps which occur in order are:

- (1) Methylation, or entry of methyl (CH₃) groups into the phenol ring in the ortho or para positions.
- (2) Condensation of two methyl groups to form an ether bridge.
- (3) Condensation between a methyl group and a phenol nucleus to form a methylene bridge (-CH₂-).
- (4) Decomposition of ether bridges (-O-) to form methylene bridges and formaldehyde, which immediately reacts via the first three reactions.

In the case of two-step resins:

(1) One molecule of formaldehyde plus two phenol nuclei will condense to form a methylene bridge (again in ortho or para positions) with elimination of water.

(2) In order to cure the novolac, which is as permanently fusible (thermoplastic), it must be further reacted with a catalyst such as hexamethylenetetramine or formaldehyde. These furnish additional methylene bridges so that the novolac ultimately becomes a rigid cross-linked thermoset via the final process described for resins.

The physicochemical state of phenolic resins during cure may be further described by defining three distinct processes:

A-stage resin (novolac): The initial condensation product (see cross-linking).

B-stage resin (resin): Cross-linking has commenced and the resin is thermoplastic, softening when hot and remaining hard and brittle at room temperature.

C-stage resin (resin): The final polymerization stage has been reached and the resin is completely thermoset (infusible and brittle).

Substitutions and Modifications

The many combinations of phenol and formaldehyde with various catalysts and curing conditions make possible a wide range of property variations in the finished thermoset resins. However, many substitutions are possible that improve the resins or eliminate undesirable properties.

A large number of phenol-related materials can be directly substituted for phenol. The property variation induced depends upon functionality, side-chain length, and other factors. A high degree of reactivity is desirable, as exemplified for instance by diphenyl acid which possesses eight reactive sites.

Commercial substitutes for formaldehyde are limited to paraformaldehyde and furfural (see Chapter II-4), but, as stated, formaldehyde is used in 95% of all phenolics produced.

Modifications include variations in batch cycle as well as changes in mole ratio, catalyst type and concentration. Equally important, however, are the complex and simple inorganic or organic compounds added to the batch to induce improvements in moisture or chemical resistance, flexibility or other specific properties. These modifiers represent a group whose effects are determined empirically, usually without pre-

terminal know-how, and their identification is in most instances kept confidential and proprietary.

To further provide interesting property variations, blends (alloys), and mixtures of phenolic resins with other polymer types such as epoxies and rubbers (both thermosetting and thermoplastic) have been made. These have made possible improved adhesion of resins to various substrates or reinforcements, and also have produced compounds with greater abrasion and wear resistance.

TESTING

In addition to tests for water (or solids) content (titration or dehydration methods), viscosity, specific gravity, etc. commonly used or described previously (Chapter II-1), several other tests which are especially applicable to phenolics have been devised. These comprise the following: two formaldehyde, novolac matter (nov), starch cure, set time, water solubility (or tolerance). Procedures for these tests are duplicated in Appendices II-3.1 to II-3.6 at the end of this chapter.

PHENOLICS AS REINFORCED PLASTICS

Phenolics resins find application as adhesives, bonding and impregnating agents, molding compounds and laminates, in coating operations, and as products. The bonding, molding compound and laminating applications are of essential importance as Reinforced Plastics and will be discussed in detail.

In the general handling and curing, and in consideration of cure properties, certain advantages and disadvantages of phenolics compared to polyesters present themselves. These may be summarized as follows:

Advantages

- (1) Phenolics may be B-staged, permitting delayed cures. Only the more expensive DAP polyesters may be B-staged.
- (2) General-purpose phenolics are 10 to 25% cheaper than polyesters on a solids basis.
- (3) Phenolics possess higher temperatures per pound than polyesters, and retain a higher percentage of original strength after long-term high-temperature exposure.

- (4) Phenolics may be specially formulated so as to provide inherent flame resistance, far superior to that for polyesters.
- (5) They exhibit good mechanical properties, and good chemical and moisture resistance.
- (6) They may be cured by heat and pressure alone and do not require complex inhibitors, promoters and catalytic additions.
- (7) Solubility in water or water and alcohol of some phenolic types permits simplified handling.
- (8) Phenolic resins have high heat-strength, minimizing tendency for warpage upon removal from molds.
- (9) Cured phenolic resins are lower in specific gravity than those for polyester resins.

Disadvantages

- (1) Phenolics have innate qualities of extreme brittleness. Attempts to plasticize phenolics (as with water-soluble glycols) to build in resiliency equivalent to that obtainable in polyester resins in degradation of cured properties.
- (2) Other problems are had with phenolics. If the dark brown color of phenolics is avoided by processing in acid baths rather than iron or steel, the brown color develops on curing, probably due to quinoids and chromophores which result from oxidation. Phenolics cannot compete colorwise with polyester, melamine, or urea resins.
- (3) Phenolics require higher pressures for cure in almost all molding or laminating operations due to necessity of countering forces caused by escaping volatiles. Only phenolic-glass laminates are molded at lower pressures.
- (4) Phenolics cure at a slower rate than polyesters. Only finished resins to which acid is added or novolac-formaldehyde resins will cure at room temperature, and these require further processing at elevated temperatures to develop ultimate properties.
- (5) Phenolics must be stored at temperatures below room temperature, and have maximum shelf lives of approximately 90 days (liquid). Powdered two-step resins to which hexamethylenetetramine has been added may be maintained at room temperature for extended periods, but tend to agglomerate to some extent.
- (6) Upon outdoor weathering, phenolic-glass laminates warp, leak, and darken further. However, during weathering they erode less than polyester resins.

Banding

Phenolic resin has been used as a binder for fiber-glass and mineral wool insulation batts for many years. A strong-base type resin is usually used by mixing into a water-based formulation together with strongly alkaline curatives and stabilizers. The formulated resinous binder is spray-applied onto the glass or wool fiber immediately after forming. The impregnated wool is collected on a moving belt which passes through a circulating air oven in which the resin is advanced through the B-stage and ultimately cured. Oven temperatures range from 225 to 450°F and the time required for curing depends upon the density and thickness of the mat to be produced. Cavity products are industrial resins (see Section III), fast-cure wood (phenol-formaldehyde binder), and compressed, higher-density densified and insulation board.

Production of the compressed insulation board employs a unique process adaptation in which fiber-glass insulation-type matting with phenolic resin applied passes through the forming stage only, and is rolled up prior to curing the resin. Hence, the resin remains in the B-stage and two or three months' shelf life is normal if storage in excess of room temperature is avoided.



Figure 12-41. Insulation of automotive head-liner made from phenolic-bonded compressed fiber-glass insulation board. (Courtesy American Moulding Corporation and Johns-Manville Fiber Glass Division)

The compressed board is ultimately processed to a finished product by molding to predetermined thickness steps as a laminate in a heated flat-plate or contained press mold. Densities after molding vary from five to ten pounds per cubic foot as compared to maximum densities of only three pounds per cubic foot for the fiber glass wool and fifteen pounds for mineral wool insulation.

Molding temperatures are maintained in the vicinity of 450°F so that more rapid cures are possible. Distillation of the resin is minimized due to the dense mold.

Originally (1931) the cured compressed board was channeled into products which utilized its properties of resiliency and vibration damping. Free-hub diameter rocket burnout steps and automotive propellers dash panels were manufactured in quantity during the period 1931 to 1934. Subsequently, concentrated development resulted in a composite panel consisting of a decorative fiber glass fabric applied to the compressed board. Both the fabric and the B-stage resin-wood combination are laid up and cured together in a contained press mold. A thin film of thermoplastic material is interlaminated and surface during the molding cycle, bonding the glass fabric to the surface of the compressed board.

A unitized, one-piece automotive head-liner and a decorative acoustical ceiling panel represent the first major-volume items utilizing the compressed-board process. Figures 12-41 and 12-42 illustrate, respectively, the automotive head-liner and the acoustical ceiling panel. Sound-damping qualities of the ceiling panel may be estimated by noting that the fiber-glass compressed board provides equivalent structural core reduction, yet it weighs only one-fourth as much as standard panels.

Additional applications involving the bonding characteristics of phenolic resin comprise use in shutters, freight materials, laundry acid cures and molds, impregnant for fiber-glass mat used in battery separation, and other miscellaneous uses.

Molding Compounds

In the present state of the art, resin manufacturers or intermediate processors supply, ready to mold, the major portion of all phenolic molding compounds used. The compounds are delivered to the molder in any of the four follow-

ing forms: granular powders, random reinforced fibers (rochels), chopped or uncutted resin-coated fabric, and resin plus fibers plasticized with solvents.

Shrinkage or difference between room-temperature dimensions of a mold and the article molded therefrom is another parameter governing successful molding, and is measurable by ASTM Method D365.

Rate of cure is an additional property requiring control, and information is generally supplied by the compound manufacturer (see Appendix II-2.4).

Special compounds require changing at a mold temperature of 170°F and subsequent increase to 250°F, with a 20 to 30-minute cycle. These are designed for superior elevated-temperature strength properties and abrasion resistance.

Old pressure molding to form a part, followed by oven curing, constitutes an original molding method still in use. Molded articles have poorer surface, lower impact, and higher water absorption than hot-molded articles, and are slightly lower in mechanical strength.

Common fillers and reinforcements for molding compounds are wood, metallic, steel, mica, clay, asbestos, graphite, nylon, rubber, glass,

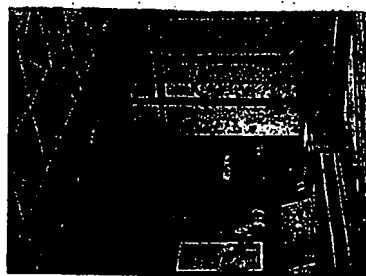


Figure 12-42. Acoustical ceiling panels made from phenolic-bonded compressed fiber-glass insulation board. (Courtesy Johns-Manville Fiber Glass Division)

ing forms: granular powders, random reinforced fibers (rochels), chopped or uncutted resin-coated fabric, and resin plus fibers plasticized with solvents. In addition, molding compounds are further classified as low shrinkage types (or powder-molding compounds containing filler only), or as high reinforcement types containing high ratios of borings or organic material to resin. Methods of compounding include use of differential rolls, mixers, extruders and choppers. Eighteen distinct phenolic molding compound types (based on performance values are the outlined. The several property types of molded phenolic materials which form or less define and usage comprise: "general purpose, impact (medium or high), electrical grade, heat-resistant, minimum bleed and other, and special-property compounds. Novolacs are usually used for preformed-type molding compounds, but resins may be employed for the impregnated-fiber-type compounds.

Actual procedures involved in final-stage pressing (curing) of phenolic molding compounds are briefly described as follows:

Preforming may or may not be necessary, as molding compounds can be fed to the cavity as powders. Random fiber or uncutted cloth types may be preformed roughly by hand or by a vibrating or piling machine. Transfer molding usually requires a preformed slug, with up to several inch-sized chips placed in the transfer pot to mold a large-sized item.

Preheating, if practicable and controllable, may effectively reduce the required time for molding.

Molding. Mold temperatures vary between 370 and 450°F. Molding pressures up to 5000 psi are required and are usually determined by heating 250 to 500 psi per inch of mold depth, or by predetermined plasticity of the compound.

The plasticity of "flow" of a molding compound is also very important in preheating whether the compound will properly fill all sections of the mold during the press cycle. ASTM Method D3731 has been proposed to measure the index of this "flow" factor. ASTM molding materials (800 psi minimum pressure required) to 2100 (for very hard (low-flow) materials (2000 minimum pressure required) are determined by measuring pressure necessary to close a standard cup mold to a specified fir-

(2) Voids are removed and the resin can be advanced by passing the impregnated sheet through a continuous drying oven. If required, cutting to size and stacking follows. However, at this stage, the sheets may be rerolled (inter-laved) for later use as a prepreg material.

(3) Curves for 20 to 25 minutes in multiple

TABLE II-32. COMPARATIVE PROPERTIES OF MOLAR CONCENTRATIONS

	Control Group	Support	Modest-Drug	Modest-Placebo	Best Outcome	Percent Positive	Percent Positive
Percent strength, 100 %	10,000	10,000	10,000	10,000	0.00	0.00	10,000
Percent strength, 50 %	5,000	5,000	5,000	5,000	0.00	0.00	5,000
Percent strength, 25 %	2,500	2,500	2,500	2,500	0.00	0.00	2,500
Percent strength, 12.5 %	1,250	1,250	1,250	1,250	0.00	0.00	1,250
Percent strength, 6.25 %	625	625	625	625	0.00	0.00	625
Percent strength, 3.125 %	312	312	312	312	0.00	0.00	312
Percent strength, 1.56 %	156	156	156	156	0.00	0.00	156
Percent strength, 0.78 %	78	78	78	78	0.00	0.00	78
Percent strength, 0.39 %	39	39	39	39	0.00	0.00	39
Percent strength, 0.19 %	19	19	19	19	0.00	0.00	19
Percent strength, 0.09 %	9	9	9	9	0.00	0.00	9
Percent strength, 0.04 %	4	4	4	4	0.00	0.00	4
Percent strength, 0.02 %	2	2	2	2	0.00	0.00	2
Percent strength, 0.01 %	1	1	1	1	0.00	0.00	1
Percent strength, 0.005 %	0.5	0.5	0.5	0.5	0.00	0.00	0.5
Percent strength, 0.002 %	0.2	0.2	0.2	0.2	0.00	0.00	0.2
Percent strength, 0.001 %	0.1	0.1	0.1	0.1	0.00	0.00	0.1
Percent strength, 0.0005 %	0.05	0.05	0.05	0.05	0.00	0.00	0.05
Percent strength, 0.0002 %	0.02	0.02	0.02	0.02	0.00	0.00	0.02
Percent strength, 0.0001 %	0.01	0.01	0.01	0.01	0.00	0.00	0.01
Percent strength, 0.00005 %	0.005	0.005	0.005	0.005	0.00	0.00	0.005
Percent strength, 0.00002 %	0.002	0.002	0.002	0.002	0.00	0.00	0.002
Percent strength, 0.00001 %	0.001	0.001	0.001	0.001	0.00	0.00	0.001
Percent strength, 0.000005 %	0.0005	0.0005	0.0005	0.0005	0.00	0.00	0.0005
Percent strength, 0.000002 %	0.0002	0.0002	0.0002	0.0002	0.00	0.00	0.0002
Percent strength, 0.000001 %	0.0001	0.0001	0.0001	0.0001	0.00	0.00	0.0001
Percent strength, 0.0000005 %	0.00005	0.00005	0.00005	0.00005	0.00	0.00	0.00005
Percent strength, 0.0000002 %	0.00002	0.00002	0.00002	0.00002	0.00	0.00	0.00002
Percent strength, 0.0000001 %	0.00001	0.00001	0.00001	0.00001	0.00	0.00	0.00001
Percent strength, 0.00000005 %	0.000005	0.000005	0.000005	0.000005	0.00	0.00	0.000005
Percent strength, 0.00000002 %	0.000002	0.000002	0.000002	0.000002	0.00	0.00	0.000002
Percent strength, 0.00000001 %	0.000001	0.000001	0.000001	0.000001	0.00	0.00	0.000001
Percent strength, 0.000000005 %	0.0000005	0.0000005	0.0000005	0.0000005	0.00	0.00	0.0000005
Percent strength, 0.000000002 %	0.0000002	0.0000002	0.0000002	0.0000002	0.00	0.00	0.0000002
Percent strength, 0.000000001 %	0.0000001	0.0000001	0.0000001	0.0000001	0.00	0.00	0.0000001
Percent strength, 0.0000000005 %	0.00000005	0.00000005	0.00000005	0.00000005	0.00	0.00	0.00000005
Percent strength, 0.0000000002 %	0.00000002	0.00000002	0.00000002	0.00000002	0.00	0.00	0.00000002
Percent strength, 0.0000000001 %	0.00000001	0.00000001	0.00000001	0.00000001	0.00	0.00	0.00000001
Percent strength, 0.00000000005 %	0.000000005	0.000000005	0.000000005	0.000000005	0.00	0.00	0.000000005
Percent strength, 0.00000000002 %	0.000000002	0.000000002	0.000000002	0.000000002	0.00	0.00	0.000000002
Percent strength, 0.00000000001 %	0.000000001	0.000000001	0.000000001	0.000000001	0.00	0.00	0.000000001
Percent strength, 0.000000000005 %	0.0000000005	0.0000000005	0.0000000005	0.0000000005	0.00	0.00	0.0000000005
Percent strength, 0.000000000002 %	0.0000000002	0.0000000002	0.0000000002	0.0000000002	0.00	0.00	0.0000000002
Percent strength, 0.000000000001 %	0.0000000001	0.0000000001	0.0000000001	0.0000000001	0.00	0.00	0.0000000001
Percent strength, 0.0000000000005 %	0.00000000005	0.00000000005	0.00000000005	0.00000000005	0.00	0.00	0.00000000005
Percent strength, 0.0000000000002 %	0.00000000002	0.00000000002	0.00000000002	0.00000000002	0.00	0.00	0.00000000002
Percent strength, 0.0000000000001 %	0.00000000001	0.00000000001	0.00000000001	0.00000000001	0.00	0.00	0.00000000001
Percent strength, 0.00000000000005 %	0.000000000005	0.000000000005	0.000000000005	0.000000000005	0.00	0.00	0.000000000005
Percent strength, 0.00000000000002 %	0.000000000002	0.000000000002	0.000000000002	0.000000000002	0.00	0.00	0.000000000002
Percent strength, 0.00000000000001 %	0.000000000001	0.000000000001	0.000000000001	0.000000000001	0.00	0.00	0.000000000001
Percent strength, 0.000000000000005 %	0.0000000000005	0.0000000000005	0.0000000000005	0.0000000000005	0.00	0.00	0.0000000000005
Percent strength, 0.000000000000002 %	0.0000000000002	0.0000000000002	0.0000000000002	0.0000000000002	0.00	0.00	0.0000000000002
Percent strength, 0.000000000000001 %	0.0000000000001	0.0000000000001	0.0000000000001	0.0000000000001	0.00	0.00	0.0000000000001
Percent strength, 0.0000000000000005 %	0.00000000000005	0.00000000000005	0.00000000000005	0.00000000000005	0.00	0.00	0.00000000000005
Percent strength, 0.0000000000000002 %	0.00000000000002	0.00000000000002	0.00000000000002	0.00000000000002	0.00	0.00	0.00000000000002
Percent strength, 0.0000000000000001 %	0.00000000000001	0.00000000000001	0.00000000000001	0.00000000000001	0.00	0.00	0.00000000000001
Percent strength, 0.00000000000000005 %	0.000000000000005	0.000000000000005	0.000000000000005	0.000000000000005	0.00	0.00	0.000000000000005
Percent strength, 0.00000000000000002 %	0.000000000000002	0.000000000000002	0.000000000000002	0.000000000000002	0.00	0.00	0.000000000000002
Percent strength, 0.00000000000000001 %	0.000000000000001	0.000000000000001	0.000000000000001	0.000000000000001	0.00	0.00	0.000000000000001
Percent strength, 0.000000000000000005 %	0.0000000000000005	0.0000000000000005	0.0000000000000005	0.0000000000000005	0.00	0.00	0.0000000000000005
Percent strength, 0.000000000000000002 %	0.0000000000000002	0.0000000000000002	0.0000000000000002	0.0000000000000002	0.00	0.00	0.0000000000000002
Percent strength, 0.000000000000000001 %	0.0000000000000001	0.0000000000000001	0.0000000000000001	0.0000000000000001	0.00	0.00	0.0000000000000001
Percent strength, 0.0000000000000000005 %	0.00000000000000005	0.00000000000000005	0.00000000000000005	0.00000000000000005	0.00	0.00	0.00000000000000005
Percent strength, 0.0000000000000000002 %	0.00000000000000002	0.00000000000000002	0.00000000000000002	0.00000000000000002	0.00	0.00	0.00000000000000002
Percent strength, 0.0000000000000000001 %	0.00000000000000001	0.00000000000000001	0.00000000000000001	0.00000000000000001	0.00	0.00	0.00000000000000001
Percent strength, 0.00000000000000000005 %	0.000000000000000005	0.000000000000000005	0.000000000000000005	0.000000000000000005	0.00	0.00	0.000000000000000005
Percent strength, 0.00000000000000000002 %	0.000000000000000002	0.000000000000000002	0.000000000000000002	0.000000000000000002	0.00	0.00	0.000000000000000002
Percent strength, 0.00000000000000000001 %	0.000000000000000001	0.000000000000000001	0.000000000000000001	0.000000000000000001	0.00	0.00	0.000000000000000001
Percent strength, 0.000000000000000000005 %	0.0000000000000000005	0.0000000000000000005	0.0000000000000000005	0.0000000000000000005	0.00	0.00	0.0000000000000000005
Percent strength, 0.000000000000000000002 %	0.0000000000000000002	0.0000000000000000002	0.0000000000000000002	0.0000000000000000002	0.00	0.00	0.0000000000000000002
Percent strength, 0.000000000000000000001 %	0.0000000000000000001	0.0000000000000000001	0.0000000000000000001	0.0000000000000000001	0.00	0.00	0.0000000000000000001
Percent strength, 0.0000000000000000000005 %	0.00000000000000000005	0.00000000000000000005	0.00000000000000000005	0.00000000000000000005	0.00	0.00	0.00000000000000000005
Percent strength, 0.0000000000000000000002 %	0.00000000000000000002	0.00000000000000000002	0.00000000000000000002	0.00000000000000000002	0.00	0.00	0.00000000000000000002
Percent strength, 0.0000000000000000000001 %	0.00000000000000000001	0.00000000000000000001	0.00000000000000000001	0.00000000000000000001	0.00	0.00	0.00000000000000000001
Percent strength, 0.00000000000000000000005 %	0.000000000000000000005	0.000000000000000000005	0.000000000000000000005	0.000000000000000000005	0.00	0.00	0.000000000000000000005
Percent strength, 0.00000000000000000000002 %	0.000000000000000000002	0.000000000000000000002	0.000000000000000000002	0.000000000000000000002	0.00	0.00	0.000000000000000000002
Percent strength, 0.00000000000000000000001 %	0.000000000000000000001	0.000000000000000000001	0.000000000000000000001	0.000000000000000000001	0.00	0.00	0.000000000000000000001
Percent strength, 0.000000000000000000000005 %	0.0000000000000000000005	0.0000000000000000000005	0.0000000000000000000005	0.0000000000000000000005	0.00	0.00	0.0000000000000000000005
Percent strength, 0.000000000000000000000002 %	0.0000000000000000000002	0.0000000000000000000002	0.0000000000000000000002	0.0000000000000000000002	0.00	0.00	0.0000000000000000000002
Percent strength, 0.000000000000000000000001 %	0.0000000000000000000001	0.0000000000000000000001	0.0000000000000000000001	0.0000000000000000000001	0.00	0.00	0.0000000000000000000001
Percent strength, 0.0000000000000000000000005 %	0.00000000000000000000005	0.00000000000000000000005	0.00000000000000000000005	0.00000000000000000000005	0.00	0.00	0.00000000000000000000005
Percent strength, 0.0000000000000000000000002 %	0.00000000000000000000002	0.00000000000000000000002	0.00000000000000000000002	0.00000000000000000000002	0.00	0.00	0.00000000000000000000002
Percent strength, 0.0000000000000000000000001 %	0.00000000000000000000001	0.00000000000000000000001	0.00000000000000000000001	0.00000000000000000000001	0.00	0.00	0.00000000000000000000001
Percent strength, 0.00000000000000000000000005 %	0.000000000000000000000005	0.000000000000000000000005	0.000000000000000000000005	0.000000000000000000000005	0.00	0.00	0.000000000000000000000005
Percent strength, 0.00000000000000000000000002 %	0.000000000000000000000002	0.000000000000000000000002	0.000000000000000000000002	0.000000000000000000000002	0.00	0.00	0.000000000000000000000002
Percent strength, 0.00000000000000000000000001 %	0.000000000000000000000001	0.000000000000000000000001	0.000000000000000000000001	0.000000000000000000000001	0.00	0.00	0.000000000000000000000001
Percent strength, 0.000000000000000000000000005 %	0.0000000000000000000000005	0.0000000000000000000000005	0.0000000000000000000000005	0.0000000000000000000000005	0.00	0.00	0.0000000000000000000000005
Percent strength, 0.000000000000000000000000002 %	0.0000000000000000000000002	0.0000000000000000000000002	0.0000000000000000000000002	0.0000000000000000000000002	0.00	0.00	0.0000000000000000000000002
Percent strength, 0.000000000000000000000000001 %	0.0000000000000000000000001	0.0000000000000000000000001	0.0000000000000000000000001	0.0000000000000000000000001	0.00	0.00	0.0000000000000000000000001
Percent strength, 0.0000000000000000000000000005 %	0.00000000000000000000000005	0.00000000000000000					

^a 43 hours at 30°C, heated at room temperature.

Specific properties of phenolic-plus laminates may be determined by consulting references 12, 13, 14, 15, 16 and 17. Military Specification MIL-B-2093 outlines properties and performance requirements for phenolic low-pressure laminating resins. A comparison is made in Table 1 of the properties of the various laminating resins. A comparison is made in Table 2 of the properties of the various laminating resins.

A problem in retransforming arises from the dis-

APPENDIX B-2.3—PHENOLIC RESIN TESTS

TEST: NONVOLATILE MATTER IN VARNISH PHENOLIC RESINS

Application of Test

1. This method is used to determine the non-volatile content of phenolic varnishes, based on an arbitrary set of conditions.

Apparatus

- a) Balance accurate to 0.001 gram.
- b) Drying dishes, stainless tin, having an inside diameter of approximately 3 1/2 inches and a height of approximately 1 1/2 inches. A standard pint tin can cover is suitable for this use.
- c) Desiccator.
- d) Oven, gravity convection, controlled at 120°C ± 1°C.
- e) Weighing bottle and stopper.
- f) Thermometer, range 0 to 200°C, graduated to 1°C.

Procedure

- a) Heat 8 drying dishes for at least 30 minutes in the 120°C oven. Cool for 15 minutes in a desiccator. Mark each dish in some manner for identification, and weigh to the nearest 0.001 gram. From the stoppered weighing bottle, weigh by difference to the nearest 0.001 gram, 1.4 to 1.6 gram of the resin solution into each

drying dish. Spread the resin sample over the bottom of the drying dish evenly. Use a slight tilting circular motion to facilitate even spreading.

- b) Within 30 minutes after preparation, place the drying dishes in the constant-temperature oven. Cool for 15 minutes in a desiccator. Weigh each dish to the nearest 0.001 gram. The dishes should remain for a period of 1 hour ± 5 minutes. At the end of the 1-hour heating period, remove the dishes and place them in the desiccator for 15 to 20 minutes. Then weigh the drying dishes with the residue immediately to the nearest 0.001 gram.

Calculation

- a) Nonvolatile matter,

$$\% = \frac{(\text{wt. of residue} + \text{dish}) - (\text{wt. of dish})}{\text{wt. of sample}} \times 100$$

Report

1. Report the average of the three determinations to the nearest 0.05%. Do not use results more than 0.05% apart. At least two results are to be used in the report.

APPENDIX B-2.4—PHENOLIC RESIN TESTS

TEST: DILUTABILITY OF WATER-SOLUBLE PHENOLIC RESINS—STANDARD METHOD

Application of Test

1. This test is used to determine the tolerance of water-soluble phenolic resins for water, without producing turbidity.

Apparatus

- a) Rubber, 600 ml.
- b) Graduated, narrow 500 ml. with glass stopper, graduated to 2 ml.
- c) Graduated, range 10 ml., graduated to 0.2 ml.
- d) Constant temperature bath, controlled at 20°C ± 0.5°C.

Procedure

- a) Fill a 600-ml beaker with water and maintain this water at a temperature of 20°C ±

- a) Cool the sample to 25°C ± 0.5°C. Using a 10-ml graduated, transfer 10.0 ml of the sample to a 50-ml graduated, and add 40.0 ml of the 20°C water to the sample. Gradually stir the mixture with a glass rod until the sample is uniform. Shake well and transfer the contents to the 500-ml graduated. Repeat this procedure twice. Mix resin and water in the 500-ml graduated by tilting the stoppered graduated back and forth until the solution is uniform. If the solution is transparent, add an additional 10.0 ml of water and mix as before. Continue the addition of water in 10.0 ml increments, mixing with the solution and always maintaining the temperature of the mixture at 20°C ± 0.5°C until the solution is

Report

- a) Report the per cent dilutability to the nearest hundred.
- b) A dilutability of over 900% is reported as infinity.
- c) If a faint turbidity should appear at one point of the dilution test, report sharply as a turbidity of water. If additional dilution is required, this fact must be reported in the result.

Notes

1. Show the water dilutability of water-soluble resins is greatly affected by the temperature of the test, the required temperature of 20°C ± 0.5°C should be strictly adhered to.

Calculation

- a) Per cent dilutability

$$= \frac{(\text{total ml water and sample}) - 50}{50} \times 100$$

APPENDIX B-2.5—PHENOLIC RESIN TESTS

TEST: STROKER CURE OF PHENOLIC RESINS, HOT-PLATE METHOD

Application of Test

1. This method is used to determine the curing time of thermosetting resins.

Apparatus

- a) Refrigeration upon, bowl 1/4 inch deep and 1 1/2 inch in diameter.
- b) Hot plate, 6 inch ± 0.5 inch surface area, heated at 150 ± 0.5°C.
- c) Mercurian wax or eubalite.
- d) Thermometer, range 0 to 200°C, graduated to 1°C.
- e) Spatula, metal, 4 inch.
- f) Timer, accurate to 1 second.

Procedure

- a) Set up the hot plate in an area shielded from drafts.
- b) Coat the hot plate with a thin film of mercurian wax. Wipe off any excess that may remain. The wax will make removal of the cured resin easier after the test is completed.
- c) Adjust the hot plate to 150 ± 0.5°C. Stir the resin thoroughly and, using the desiccator spoon, place a small amount of the resin in the center of the hot plate. At the same time, start the stopwatch and spread the resin with a circular motion of

- a) the spatula. Use only enough pressure to bring the spatula into a flat position on the hot plate. Gradually spread the resin over an area about five inches in diameter. If the resin pulls up on the top of the spatula, do not try to return it to the plate surface. It may be scraped off on an edge of the hot plate if necessary.
- b) Stop the stopwatch and record as the cure begins the time at which the surface of the resin is flat. The curing time is the time from the time the resin is spread on the hot plate surface. When the spatula is flat across a spread resin the resin either "cures" or else offers very little resistance to the spatula's motion.
- c) Check the temperature to make sure it has not changed during the test.
- d) At least two checks agreeing within a range of ± 5% from the average of both tests should be made.
- e) Clean the hot plate by scraping with the brass spatula and polish with emery cloth, if necessary, immediately after completion of the test. The quicker the resin is removed from the surface, the easier the task will be. If the surface is too clean, erroneous cure times will result.

Report

1. Report the time to cure in seconds and the test temperature in degrees centigrade.

APPENDIX D-2.6—PHENOLIC RESIN TESTS

TEST: SET TIME OF PHENOLIC VARNISHES.

Applications of Test:

1. This method is used to determine the relative rate of polymerization of various monomers at a given temperature.

Introduction

2. a) Agitator, a 19-tooth length of 8-mm glass rod sealed to a 8-cm length of 9-mm glass rod.
- b) Balance, accurate to 0.01 gram.
- c) Constant temperature bath, controlled at $145^{\circ}\text{C} \pm 1^{\circ}\text{C}$.
- d) Laboratory motor, 350 rpm, with clutch to 81 9-cm rod.
- e) Test tubes, Pyrex, 150 mm \times 20 mm.
- f) Test tube clamp.
- g) Timer, accurate to 0.1 second.

expansion

2. a) Attach the glass-red agitator to the bottom of the laboratory motor. Weigh to the nearest 0.1 gram, 2.4 to 2.6 gm of the resin sample into a test tube. Slip the mounted agitator into and into the test tube. Lift the test tube up until the agitator touches the test tube bottom lightly. Center the agitator in the test tube, then clamp the test tube into this position tightly.

Notes

6. In some cases, transfer of the resin to the agitator is not complete. The change from liquid to an amber, gel-like solid and the wobbling agitator still hold true and are the best means to detect the end point.

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Chapter II-3

EPOXY RESINS

INTRODUCTION AND DEFINITIONS

Epoxy resins are characterized by the presence of oxirane or epoxide groupings



These may be present in the raw materials reacted to form the resin (conventional or novolac type) or may be formed during the reaction (epoxidized polyolefins type). Reactive hydroxyl groups and vinyl unsaturation also appear in epoxide epoxy resin molecules.

Whether the resin, aromatic or aliphatic polymer molecules containing an average of more than one of the epoxide groups comprise epoxy resins. The groups may occupy various positions within the molecule, such as terminal, internal, ring situated, glycidyl, etc.

Cure may be established using materials chosen as hardeners or curing agents. These react to polymerize epoxy resins through either one of two methods: (a) catalytic means in which the epoxide groups on the resin molecules interact (catalytic example—boron trifluoride), or (b) by cross-linking in which epoxidizing molecules unite with the epoxy resin molecules bearing part of the cured resin network (example—amine curing agents).^{1,2} In both cases, the epoxide groups are opened, and subsequently a well-built polymer structure is formed. The three-membered epoxide ring is of interest due to its high reactivity potential, contributing to the fact that epoxy resins per se have exhibited interesting and superior cured properties. This is true primarily because, during cure, no rearrangement occurs in the backbone of the resin molecule; the reactive epoxide groups usually being held on the cured molecule as appendages.

Table II-3.1 presents a classified summary of

the three major types of epoxy resins of commercial significance: (a) epichlorohydrin-bisphenol A (conventional), (b) epoxy novolac, and (c) epoxidized polyolefin resin. Curing agent or hardener systems for the conventional epoxy are described and their properties and optimum reaction quantities summarized in Table II-3.1. Curing agents for the novolac and polyolefin epoxies are summarized in Table II-3.1.

The behavior and handling of epoxy resins will be clarified by noting the following definitions: *Epoxide Equivalent* represents the accepted method of expressing epoxy resin functionality, and is the weight in grams of the amount of resin which contains one gram-molecular equivalent of epoxy (usually determined by IEC reaction and titration, and supplied by the resin manufacturer). *Epoxy Value* is another expression of epoxy resin functionality, and is defined as the number of epoxy groups contained in 100 grams of resin. Epoxy value is equal to the epoxide equivalent divided into 100. In order to determine required resin and curing-agent combining quantities, the units equivalent is first determined by:

$$\begin{array}{l} \text{Molecular weight of the resin curing agent} \quad 0 \\ \text{Number of reactive hydrogen atoms} \quad \text{in the resin molecule} \quad 100 \\ \hline \text{The required amount of curing agent (Z phr)} \text{ is then determined by equating the ratio of:} \\ \text{epoxide equivalent to (Z phr)} \quad 0 \end{array}$$

As an example, diethylene triamine, H₂N—CH₂—CH₂—NH₂, has a molecular weight of 103 and five reactive hydrogens are contained in the molecule, thus providing an amine equivalent of 103.3/5, or 20.7. Then, for a

Foot continued on p. 8.

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TABLE II.2.1 CLASSIFICATION OF COMMERCIALY SIGNIFICANT EPOXY RESIN TYPES

	Conventional Epoxy Resins ^a		Epoxy Novolac Resins ^b					Specialized Polyethers ^c																									
1. Chemical composition and/or classification	Diglycidyl ether of bisphenol A with only smaller amounts of higher mol. wt. homologs		High mol. wt. homologs of diglycidyl ether of bisphenol A																														
2. Organic resin materials	Bisphenol A, epichlorohydrin		Novolac resins, epichlorohydrin					Oxide plus peroxide acid																									
			<table><tr><th colspan="2">Thermal</th><th rowspan="2">Mol. Wt. Range</th><th rowspan="2">Glass Transition Temp., °C.</th><th rowspan="2">Softening Point, °C.</th></tr><tr><th>Hardened = Resin</th><th>Hardened = Resin</th></tr><tr><td>1.53-1 = 750 (approx)</td><td>1.53-1 = 750 (approx)</td><td>1</td><td>133</td><td>8</td><td>170</td></tr><tr><td>1.53-1 = 800 (approx)</td><td>1.53-1 = 800 (approx)</td><td>2</td><td>133</td><td>8</td><td>170</td></tr><tr><td>1.53-1 = 1370 (approx)</td><td>1.53-1 = 1370 (approx)</td><td>3</td><td>133</td><td>8</td><td>170</td></tr></table>					Thermal		Mol. Wt. Range	Glass Transition Temp., °C.	Softening Point, °C.	Hardened = Resin	Hardened = Resin	1.53-1 = 750 (approx)	1.53-1 = 750 (approx)	1	133	8	170	1.53-1 = 800 (approx)	1.53-1 = 800 (approx)	2	133	8	170	1.53-1 = 1370 (approx)	1.53-1 = 1370 (approx)	3	133	8	170	
Thermal		Mol. Wt. Range	Glass Transition Temp., °C.	Softening Point, °C.																													
Hardened = Resin	Hardened = Resin																																
1.53-1 = 750 (approx)	1.53-1 = 750 (approx)	1	133	8	170																												
1.53-1 = 800 (approx)	1.53-1 = 800 (approx)	2	133	8	170																												
1.53-1 = 1370 (approx)	1.53-1 = 1370 (approx)	3	133	8	170																												
3. Molecular weights	Actual (based on mol. wt. data) Theoretical (as 1 (bis) to 2 (ep) cured units)	Actual (based on mol. wt. data) Theoretical (as 1 (bis) to 2 (ep) cured units)						Typical Examples ^d (Pounded) 500 pps. polyethers in 500 pps. toluene 50 pps. glycidyl ether in 50 pps. toluene 100 pps. glycidyl ether in 100 pps. toluene 100 pps. hydrogen peroxide																									
4. Reaction catalysts	NaOH (0.5 mole/mole bisphenol A) or other catalysts used to neutralize the HCl which is formed.		NaOH (0.5 mole/mole bisphenol A) or other catalysts used to neutralize the HCl which is formed.					Low-molecular weight																									
5. Reaction procedure	Bisphenol A and epichlorohydrin solution are stirred together at 100°C (approx) in N ₂ atmosphere; NaOH solution added at slow rate to bring solution neutral; the organic layer (product) is separated, dried with sodium sulfate and vacuum distilled. ^e		Bisphenol A and epichlorohydrin solution are stirred together at 100°C (approx) in N ₂ atmosphere; NaOH solution added at slow rate to bring solution neutral; the organic layer (product) is separated, dried with sodium sulfate and vacuum distilled. ^e					A polyether such as bisphenol A is first polymerized and then reacted with peroxide acid to produce the specialized polyether acid solution. The peroxide acid may be either formed in situ or generated externally and added to the batch.																									
6. Reaction type	Dehydrohalogenation		Dehydrohalogenation					Peroxide acid epoxidation																									
7. Form of reacted resin	Liquid		Solid					Liquid																									
8. General resin properties	Light yellow 100-150 pps @ 177° Aqueous 1:1 100-200 Most of organic solvents		Yellowish — 100-200 Ketones, alcohols, aromatic hydrocarbons Room temperature to 100°C One year					Light yellow 100-200 pps @ 177° 1:1 (approx) 100-200 Ketones, alcohols and aromatic hydrocarbons — One year																									

[illegible]

TABLE II-3.3. CURING AGENTS FOR CONVENTIONAL TYPE EPOXY RESINS

Type of Resins	Typical Curing Agent Properties	Characteristics of Resins-C. A. System	Material	Examples		
				PER for Curing Heat Deflection Temp.	RT Pot Life or Cure Time & Temp.	Heat Deflec- tion Tempera- ture (after full cure)
1. Primary aliphatic polyamines ^{a, b}	Low-viscosity liquids; disagreeable odor; irritating vapor; skin sensitizers.	Promote rapid cure at R. T. with short pot life and high exotherm; postcuring increases heat-deflection temperature; improves chemical resistance and electrical properties.	Diethylene triamine	12	20 min	177
			Triethylene tetramine	12	20 min	245
			Diethylaminoethylamine	8	RT (5 hr not cured)	210
			Dimethylaminoethylamine	4	Cure: 2 hr-250°F Gel: 6 hr	245
2. Modified primary aliphatic polyamines	Liquids with viscosities similar to conventional resins; odor less noxious than No. 1; lower skin-sensitizing potential than No. 1.	Provide more convenient mixing ratios; faster curing, somewhat lower irritation potential; lower vapor pressure; tend to reduce physical & chemical properties.	Amine resin adducts	24	20 min	157
			Amine ethylene oxide adducts	20	15 min	194
			Cyanosilylation product	22.5	42 min	180
			Amine phenol (proprietary mixture)	16.5	11 min	233
3. Cyclic aliphatic amines	Low-viscosity liquids; vary from mild to strong vapors.	Long pot life; low exotherm possible; postcure usually required.	Piperidine	10	Thick gel: 2-6 hr Set: 22-48 hr	183
			N-aminocetyl piperazine	18	18 min	233
4. Aromatic amines	Solids (some proprietary aromatic amines are liquids); irritating vapor.	Higher heat-deflection temperatures than aliphatic amines; can be used for B-staging.	Metaphenylene diamine ^a	21	0-18 hr	227
			Diamine diphenyl sulfone ^a	20	Cure: 1 hr-300°F	247
			Dicyandiamide (with solid resins)	4	Cure: 1/2 hr-345°F	—

5. Tertiary amines	Low-viscosity liquids; mild odor; low skin-sensitizing potential.	Long pot lives; can be used as accelerators for polyamides and anhydride cures.	Dimethylamino ethanol	4	Thick gel: 0-6 hr Set: 0-18 hr	224
			Benzyldimethylamine	9	Thick gel: 6 hr Set: 0-18 hr	185
6. Latent curing agents	Liquids and solids.	Long pot lives; cure activated by heat.	Boron trifluoride-monoethylamine complex	2-4	7 to 30 days	—
			Triethanolamine borate	—	Cure: 1 hr-250°F	233
7. Polyamides ^{a, b}	Medium to high-viscosity liquids; mild odor; low skin-sensitizing potential.	Impart flexibility to resins when cured.	Reaction product of ethylene diamine and the dimer of linoleic acid	64	150 min	220
8. Acid anhydrides ^{a, b}	Solids or liquids; corrosive and some are lachrymatory, but have low skin-sensitizing potential.	High heat-deflection temperatures; high-temperature resistance; superior electrical properties; require elevated temperature cures.	Phthalic anhyd.	40-60	Cure: 3 hr-300°F	190
			Maleic anhyd.	—	—	—
			Dodecylsuccinic anhyd.	120-150	Cure: 6 hr-300°F	168
			Chlorosulfonic anhyd.	100-120	Cure: 3 hr-320°F	256
			Pyromellitic dianhydride ^a	FMDA- (15-21)	Cure: 24 hr-320°F	275-300
			and Maleic anhyd. mixtures Hexahydrophthalic anhyd. Nadic methyl anhyd.	MA-(19-27) — 60	Cure: 2.5 hr-225°F	— — 424

^a Room temperature pot lives given for 100-gm epoxy resin plus hardener; equivalent weights of resin = 100.

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ThreeBond TECHNICAL NEWS

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19

One-Part Epoxy Resin

Introduction

In addition to two-part epoxy resin, one-part epoxy resin has a wide range of applications. However, it seems that the product has not readily been and accurately understood by many people.

According to the survey conducted internally, one-part epoxy resin ranked high in both the "salable" and "difficult to sell" groups, giving a rather puzzling result. After all, though this is my own interpretation, sellers and buyers who have a

certain degree of knowledge and understanding of one-part epoxy resins can select and use them, while those who consider it difficult to sell the resins may not understand the versatility and wide range of applications of epoxy resin.

This issue of the newsletter describes one-part epoxy resin, which has various properties and a wide range of uses, in order to increase understanding of the resin.

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1. Summary

One-part epoxy resin has some commonalities with two-part epoxy resin. For example, they use the same epoxy resin, which is the fundamental ingredient thereof, and have employed very similar methods of improvement and development. In addition, the one-part technique is primarily dependent on the curing agents used. Therefore, the compounding techniques described in the present report should be understood as regarding general epoxy-resin compounds. Epoxy resin is characterized by the high degree of flexibility in its compounds due to its stability. Various compound techniques have been suggested and discussed for exploiting the flexibility and other good properties of the basic types of epoxy resin. This report describes the basic properties of the epoxy resin and the ingredients of the compounds and the roles thereof, and introduces the properties and uses of one-part epoxy resin.

2. Demand for epoxy resin in various fields

As shown in Table 1, there is demand for epoxy resin in a wide range of fields, including paints and electrical components. As a trend over the past

decade, the focus of the demand has shifted from general paints to automobile paints, and then to electrical components. In particular over the past few years, there has been increasing demand for the resin as an encapsulating material of IC and LSI for electrical machinery such as FA and OA appliances.

3. What is epoxy resin?

The term "epoxy resin" is a generic name for compounds that have two or more oxirane rings (epoxy groups) in one molecule, and are cured three-dimensionally by a suitable curing agent. However, in most cases, the term refers to bisphenol-A diglycidyl ether (DGEBA), which is formed by the reaction between bisphenol A and epichlorohydrin, which currently commands a 75% share of the epoxy-resin market. Of the products of Three Bond, 50% to 60% of one-part epoxy resin and more than 90% of two-part epoxy resin are based on DGEBA or compounds containing DGEBA. Therefore, DGEBA is synonym for epoxy resin.

The following section describes the structure and performance of epoxy resin, using DGEBA as a representative example.

Table 1. Delivery quantity of epoxy resin organized by use
(year on year (%)) 87-01-26

Uses \ Year		54		55		56		57		58		59	
Paints	Cans	5,643		4,973	88	6,378	128	5,836	92	7,234	124	8,258	114
	Automobiles			6,458	157	7,808	121	9,595	123	10,514	110	11,534	110
	Ships	3,739		4,929	132	7,533	153	7,496	100	6,888	92	7,572	110
	General purposes	11,191		10,578	95	10,153	96	9,713	96	10,974	113	13,412	122
	Total	24,676		26,938	109	31,872	118	32,640	102	35,610	109	40,776	115
Electrical components	Laminates	7,118		7,364	103	9,982	136	10,362	104	14,142	136	20,864	148
	Casting	5,282		5,367	102	4,574	85	3,658	80	4,079	112	5,266	129
	Others	2,231		2,260	101	3,413	151	3,652	107	5,483	150	11,122	203
	Total	14,631		14,991	102	17,969	120	17,672	98	23,704	134	37,252	157
Civil construction		6,901		6,558	95	7,411	113	8,002	108	9,446	118	9,469	100
Adhesives		3,582		3,659	102	3,832	105	3,609	94	3,731	103	3,882	104
Others		6,404		6,407	100	5,296	83	4,778	90	6,238	131	7,646	123
Domestic demand total		56,194		58,553	104	66,380	113	66,701	100	78,729	118	99,025	126
Export		915		902	99	568	63	866	152	1,330	154	1,729	130
Grand total		57,109		59,455	104	66,948	113	67,567	101	80,059	118	100,754	126

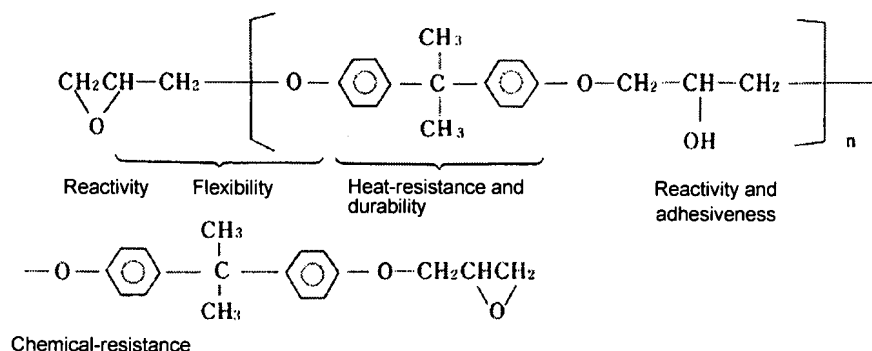


Fig. 1. Structure and properties of epoxy resin

The excellent properties of epoxy resin, such as durability and adhesiveness, depend largely on its structure. Fig. 1 shows the relationship schematically.

- 1) The epoxy groups at both terminals of the molecule and the hydroxyl groups at the midpoint of the molecule are highly reactive, allowing room-temperature and high-temperature curing using suitable curing agents, and a wide range of modifications. In addition, the resin is cured by ring-opening polymerization, and as a result has a smaller
- degree of cure shrinkage than other thermosetting resins.
- 2) The ether linkages included in the main chain improve the chemical-resistance and elasticity.
- 3) The benzene rings in bisphenol A provide chemical-resistance, adhesiveness, durability, heat-resistance and excellent electrical properties.
- 4) The coexistence of hydrophilic groups with hydrophobic groups in the molecule significantly increases the adhesion to various adherends.

60		61•Breakdown								61•Total	
		1 ~ 3		4 ~ 6		7 ~ 9		10~12			
8,327	101	2,051	93	2,697	116	2,397	127	2,279	119	9,424	113
12,473	108	2,988	101	3,095	91	3,013	100	3,103	100	12,199	98
7,437	98	1,411	73	1,584	78	1,515	85	1,514	88	6,024	81
13,122	98	3,294	104	4,100	121	3,561	113	3,497	103	14,452	110
41,359	101	9,744	95	11,476	103	10,486	107	10,393	103	42,099	102
18,652	89	4,436	100	5,973	133	5,453	110	5,791	121	21,653	116
5,565	106	1,663	121	1,873	136	1,898	139	2,142	148	7,576	136
10,849	98	3,215	102	4,044	144	4,130	193	3,689	135	15,078	139
35,066	94	9,314	104	11,890	137	11,481	136	11,622	130	44,307	126
9,349	99	2,210	92	2,017	96	2,347	96	2,273	95	8,847	95
4,059	105	1,019	105	1,358	138	1,316	133	1,478	133	5,171	127
7,768	102	2,007	95	1,751	97	1,867	101	1,925	97	7,550	97
97,601	99	24,294	98	28,492	115	27,497	117	27,691	113	107,974	111
1,423	82	583	139	521	180	420	111	437	130	1,961	138
99,024	98	24,877	99	29,013	116	27,917	117	28,128	113	109,935	111

As described above, many properties are ascribable to the structure, but such properties are largely dependent on the curing agents that cause the curing reaction, resulting in wide selectivity of the epoxy resin.

4. Compounding ingredients of epoxy-resin and roles thereof

As shown in Table 2, regardless of whether it is one-part or two-part, epoxy resin is rarely used alone as an epoxy-resin material, but rather is used in the form of compounds containing various

modifiers and diluents in order to impart the resin's desirable properties, such as strength, flowability, and heat-resistance.

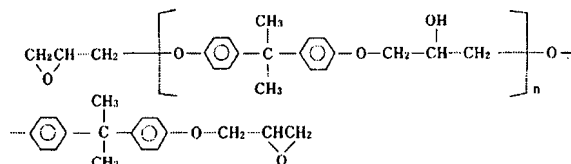
In addition to the agents described below, various agents can be mixed with epoxy resin. In such cases, epoxy resin causes remarkably less gelation and reaction inhibition than other reactive resins, which gives a significant advantage to the resin in the creation of compounds and allows anyone to make such compounds.

Table 2. Compounding ingredients of epoxy-resin and roles thereof

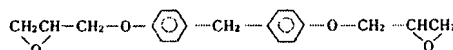
Constituents	Ingredients	Roles
Resin content	Epoxy resin	The bisphenol-A type is common. However, there are many other types of epoxy resin having different properties.
	Curing agents	Curing agents react with epoxy groups to form a three-dimensional network structure by crosslinking.
Modifying ingredients	Elasticity agents	Elasticity agents elasticate compounds to improve their peeling strength and extensibility, e.g., elasticizers and epoxy modifying resins.
	Shock-resistant agents	Shock-resistant agents eliminate brittleness from epoxy resin to prevent cracks and decrease distortion.
	Fillers	Fillers increase the weight in order to decrease costs and improving various types of mechanical strength, e.g., calcium carbonate and talc.
	Heat-resistant agents	Heat-resistant agents increase the heat-resistance and heat-deformation temperature through the use of multi-sensual types of epoxy resins such as novolac epoxy resin.
	Diluents	Diluents reduce viscosity and improve flowability and permeability. Reactive diluents having epoxy groups and nonreactive diluents having no epoxy group are available.
	Thixotropic agents	Thixotropic agents impart thixotropy to compounds in order to control flowability and increase viscosity.
	Other agents	Pigments, coupling agents, defoaming agents, leveling agents, etc.

4-1. Major types of epoxy resin

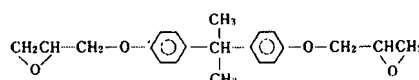
Bisphenol-A type (DGEBA); Commonly used



Bisphenol-F type; Characterized by having low viscosity



Bisphenol-A D type; Having intermediate characteristics between those of the DGEBA and bisphenol-F types



Most epoxy resins are composed on the basis of the above three types of resin. There are many other types of epoxy resins; however, most are not adaptable to a wide variety of applications, and rather are intended for special purposes such as modifications and improvements to heat-resistance and elasticity.

4-2. Various curing agents

Like epoxy resin, there are various types of curing agents for epoxy resin. In fact, there are so many types that they cannot be covered in this report; therefore, only the latent curing agent for one-part epoxy resin is described in this section.

The types of latent curing agents are classified as shown in Table 3. Including our products, those that are commercially available are primarily of the thermosetting type. Most thermosetting curing agents are of the dissolution-reactive type.

Table 3. Classification of latent curing agents

Activation means	Phenomena	Curing agents
Heat activation	Ionic reaction	Lewis-acid complexes (BF ₃ -ME-A, etc.)
	Dissolution	Dicyandiamide Modified imidazole, organic acids Hydrazides, DCMU
	Decomposition	Amine-imide compounds
	Elution Microcapsules	Molecular sieves
Light (UV)	Decomposition	Aromatic diazonium salts, diallyl iodonium salts, triaryl sulfonium salts
Moisture	Decomposition	Ketoimine
	Elution	Molecular sieves
Pressure	Microcapsules	

Using dicyandiamide as a representative example, the following section describes the characteristics

and properties of thermal-dissolution reactive curing agents.

<Dicyandiamide and derivatives thereof>

Dicyandiamides are crystals with a high melting point of 207°C to 210°C. When dispersed in epoxy resin in the form of fine powder, they will have a pot life of 6 to 12 months, and will remain stable for a greater length of time than imidazole. Four to ten parts of them are added to DGEBA.

Dicyandiamides require heating at 160°C to 180°C for one hour to several hours for curing, and generate a large quantity of heat upon curing. They tend to sediment due to their high specific gravity, and thus are not suitable for casting. They are used for coating, adhesion, and lamination.

In many cases, to decrease the curing temperature, which is a weakness of dicyandiamides, an accelerating agent is added, as shown in the following example of compound, in order to accelerate curing at a lower temperature. New accelerating agents have actively been developed.

<Example of compound>

DGEBA 100 * H₂N—C—NH—CN
DICY (dicyandiamide*) 8 ||
Dimethyl urea 3 NH

<Properties of the compound>

Curing conditions 120 °C × 30 minutes
Shearing strength 150 kg/cm²
Glass transition point 125 °C

The compound has found a wide range of applications: as an adhesive in electric and electronic applications, as an encapsulating material for terminals due to the fact that it does not cause metal corrosion, as a structural adhesive due to its

strong adhesiveness, and for pre-preg and powder coating due to its low cost.

4-3. Elasticity and shock-resistant agents

Despite its high strength, (cured) epoxy resin has the problem of brittleness due to its poor elasticity. One-part epoxy resin, when it has not been particularly elasticated, has shearing adhesive strength of 150 to 200 kgf/cm², which is relatively high for an adhesive; however, it has peeling adhesive strength of 0.5 to 1 kgf/25 mm width in a T-peel test, which is equivalent to that of instant adhesives. This is due to the fact that the cured resin is relatively low in extensibility. If this insufficiency is redressed by an elasticity agent, the resin may have shearing adhesive strength of 250 kgf/cm² or higher, and peeling adhesive force of 20 kgf/25 mm width in a T-peel test.

The elasticated agents are described below.

The purposes of adding elasticated agents include the following: 1) improvements in mechanical strength, 2) prevention of cracks due to thermal distortion, and reduction of distortion, and 3) improvements in adhesiveness, particularly

improvements in peel strength by imparting elasticity to disperse stresses.

The method of compounding elasticated agent is as follows: an elastic structure is introduced to the main chain polymer, side chain or terminal of a bisphenol type resin (see Fig. 2). However, the introduction of polymers having a rubber structure or a straight chain inevitably causes a significant increase in the viscosity of the material and deterioration of the properties of the material, such as heat-resistance, due to the decrease in the crosslinking density.

To avoid such deteriorations in properties, a special elasticated agent, carboxyl-terminal butadiene-acrylonitrile copolymer liquid rubber (CTBN), may be added. CTBN has mutual solubility with epoxy resin, but does not have it with cured epoxy resin and therein forms a dispersed rubber particle phase, and serves as a cushioning material to prevent cracks (see Fig. 3). This elasticated agent is said to provide elasticity without deteriorations in properties, due to the fact that it does not remain in the epoxy-resin layer.

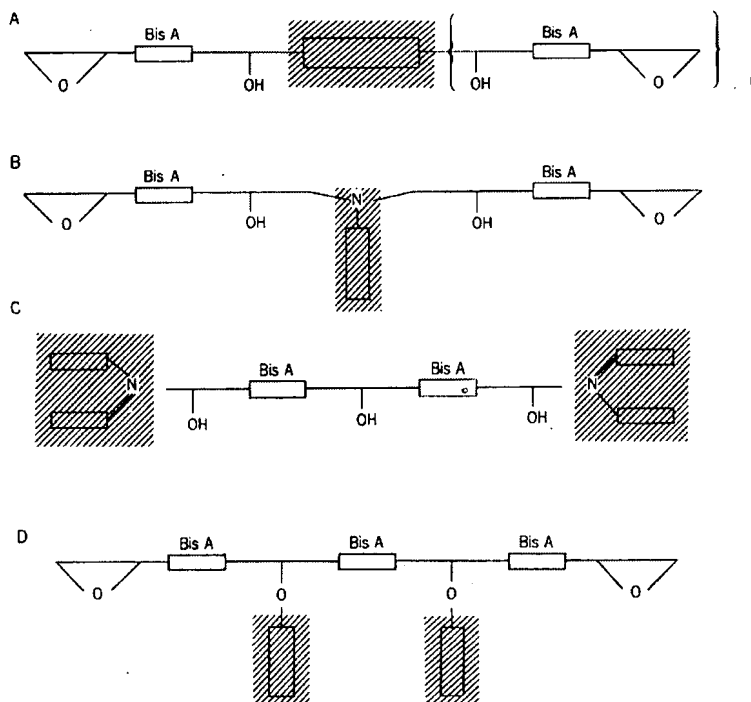


Fig. 2. Schematic structure of modified resins

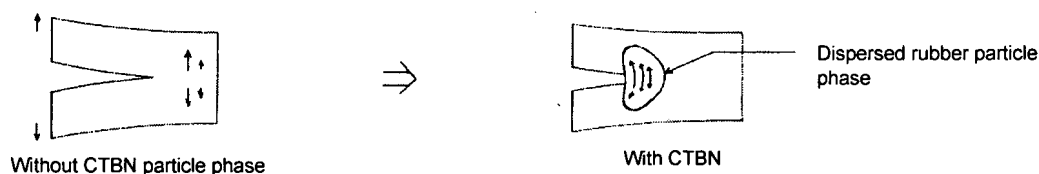


Fig. 3. Effect of CTBN

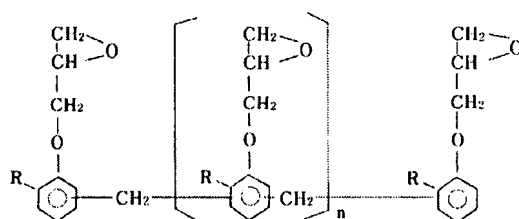
4-4. Heat-resistance improvers

The heat-resistance of compounds depends primarily on the epoxy resin contained therein. In one-part epoxy resin, the usable curing agents are limited, and thus the heat-resistance depends primarily on the type of selected epoxy resin.

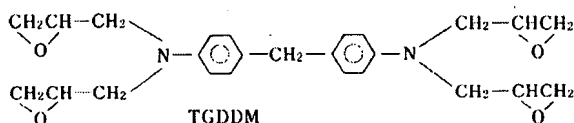
It can be generally concluded that improvements in crosslinking density contribute to improvements in heat-resistance, and thus resins with a short distance between epoxy groups, or multifunctional types of epoxy resin are commonly used.

Representative examples are given below.

Novolac epoxy resin



Glycidyl amine resin



Glycidyl ether resin

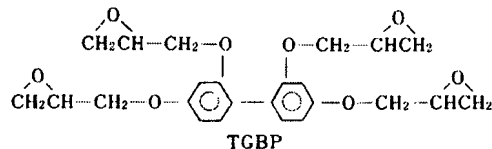


Fig. 4. Representative heat-resistance agents

4-5. Fillers

Fillers tend to be regarded merely as bulking agents, but their roles cannot be neglected due to the fact that increasingly rigorous properties are required of epoxy resin. It is therefore necessary to select and add appropriate fillers.

The effects of fillers include the following:

- 1) Improvements in mechanical strength
- 2) Reduction in thermal distortion and dimensional change
- 3) Improvements in electrical properties, particularly insulating and dielectric properties
- 4) Cost reduction due to the increase in weight
- 5) Improvements in fire retardancy

6) Improvements in heat conductivity

4-6. Diluents

As previously mentioned, when various materials are added to epoxy resin in order to improve its properties, the viscosity of the composition correspondingly increases. Bisphenol-A-type epoxy resin itself does not have low viscosity, and thus it inevitably requires adjustment (reduction) of its viscosity. For this purpose, diluents are used.

The influence of diluents on performance must be minimized, and thus the preferably used fillers are those that can have a significant effect with as small amounts as possible. One-part epoxy resin requires diluents having a low vapor pressure, as it undergoes a heating process.

Diluents fall into two types: reactive ones having epoxy groups and unreactive ones having no epoxy group. Most one-part epoxy resins are used reactive diluents, as unreactive diluents serve as a plasticizer in the cured resin. Fig. 5 shows the major diluents. Their handling requires caution, as they have a low molecular weight and readily permeate through the skin to cause irritation.

4-7. Thixotropic agents

Thixotropy is a property of liquids containing flocculating components. Flocculating components are destroyed by repeated stirring and the liquids show flowability; however, once stirring is stopped, the components reflocculate and the liquids return to the nonflowable state.

This property is required in applications in which sagging causes a problem, such as the thick coating of paints and the adhesive sealing of gaps. Commonly used effective thixotropic agents include silica fine powder (Aerosil), and colloidal hydrated aluminum silicate/organic complex (Orben).

However, the effect varies among thixotropic agents. Some exert their effect in heating, and others disappear in heating, become ineffective when cured, or deteriorate over time. Their selection is difficult even for experts.

5. Major functions and uses of one-part epoxy resins

Table 4 lists the major properties and uses of one-part epoxy resin, and Photograph 1 shows examples of the usage of one-part epoxy resin.

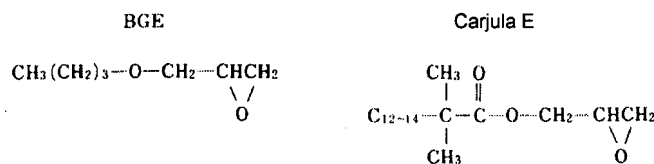
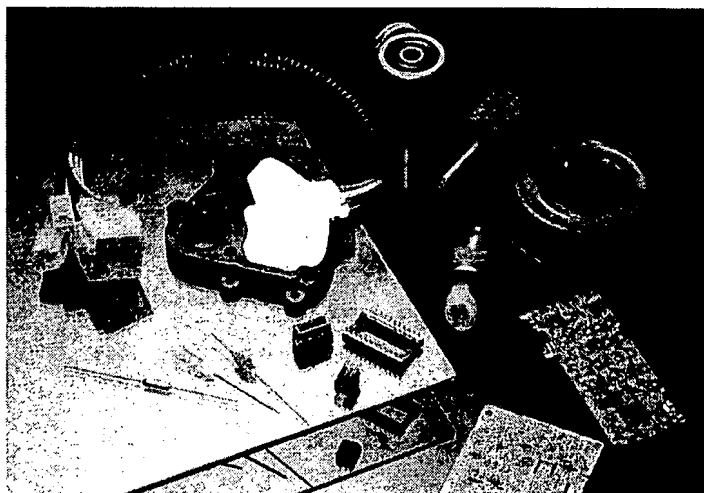


Fig. 5 Representative reactive diluents

Table 4. Major properties and uses of one-part epoxy resin

Properties	Uses	Characteristics	Product name ("TB" is an abbreviation for Three Bond.)
Heat-resistance	(1) Impregnating fixation of armature coils	Moderate impregnation properties and strength with heating at 160 °C or higher Resistance to continuous heating at 220 °C	TB2068K, TB2068H TB2064C
	(2) Heat-resistant adhesion	Glass transition temperature of 170 °C, strength with heating 200 °C, 50 kgf/cm ² , peeling strength of 14 kgf/25 mm width	TB2064C
	(3) Adhesion of motor magnets	Moderate flowability, strength with heating at 150°C or higher	TB2068M
Dimensional stability	(1) Encapsulation of heads and electrical components	Low coefficient of thermal expansion, high moisture-resistance, high purity, resistance to P.C.T. (pressure cooker test)	TB2071B
Thixotropy	(1) Antisagging, temporal adhesion of chips, fixation of coil terminals	High thixotropy, screen printability Fast curing at 150 °C, curing in one to two minutes	TB2065, TB2065M
	(2) Terminal seal for prevention of penetration	Moderate flowability, curing at a low temperature of 80 °C to 100 °C	TB2062B, TB2062D
	(3) Joint sealants	High thixotropy, high viscosity	TB2065, TB2062K
Fast curing	(1) Adhesion of syringe needles	Moderate permeability, white cured substance, curing at 150 °C in one to three minutes	TB2062D, TB2065L
	(2) Coating of stepping motors	Curing at 150 °C in one to three minutes, machinability	TB2065, TB2065C
Machinability	(1) Joint sealants for bus bodies	High shock adhesive force, slump property, and machinability	TB2063C
Impregnation	(1) Low-viscosity impregnating adhesion, impregnation of cut cores	Low viscosity, long shelf life	TB2076, TB2076C
	(2) Potting agent for small coils	Low viscosity, low shrinkage ratio	TB2071C
Elasticity	(1) Thermal shock, adhesion of motor magnets	Absorption of the thermal distortion of magnets/yokes, prevention of cracks in vibration-absorbing magnets	TB2064, TB2064B
	(2) Terminal seal for halogen-lamp	Thermal shock, conformity to terminal bending, adhesion to engineering plastics	TB2064
	(3) Adhesion of headlights (iron/glass)	Rubber elasticity	TB2067E, TB2067F TB2067D
Structural adhesion	(1) Adhesion of automobile hemming	High adhesive strength, peeling adhesive force	TB2068G
	(2) Adhesion of joints in chainsaw fuel tanks	High adhesive strength, peeling adhesive force	TB2063, TB2063D
Filling adhesion	(1) Potting of inhibitor switches	Moderate flowability, heat-resistance, weather-resistance	TB2068M, TB2068P TB2068I, TB2063J
	(2) Adhesion sealing of plastic cases	Moderate permeability, soldering heat-resistance	TB2062C, TB2062J
	(3) Encapsulation of printer heads	Moisture-resistance, flowability, low-temperature fast-curing property	TB2065E, TB2065F



Photograph 1 Examples of the usage of one-part epoxy resin

Conclusion

Three Bond has been selling one-part epoxy resin for more than ten years. In that time, we have developed various grades of products, such as a simple compounds composed of a bisphenol-A-type epoxy resin, dicyandiamide, and a filler, and those containing a low-temperature active curing agent for curing at 80 °C, as well as those comprising a heat-resistant resin to achieve high heat-resistance and those allowing a peeling adhesive force of 10 kg/25 mm width or more through rubber modification. The performance of these products has been proven.

Thanks to an increase in the demand for one-part epoxy resin and the development of various functional materials as a result of the efforts of material manufacturers, we have successfully developed proven products. We will continue to work to expand the possibilities of one-part epoxy resins.

Yukimasa Osumi
Adhesive laboratory
R&D Laboratory

ThreeBond
TECHNICAL NEWS

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Terate® Polyols

- [Aromatic Polyols From the Complete Polyester Resource](#)
- [A Leader in the Industry](#)
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- [Availability and Reliability](#)
- [Customer Service, Sales, and Technical Information](#)

Aromatic Polyols From the Complete Polyester Resource



KoSa offers a diverse line of Terate® aromatic polyester polyols for use in polyurethanes. Our polyols are available in a wide variety of equivalent weights and properties to allow for formulation flexibility. Processes using Terate polyols achieve the rigorous physical and flammability properties required in many rigid polyurethane (PUR) and polyisocyanurate (PIR) foams. The high aromaticity of Terate polyols, along with their low cost, makes them extremely desirable for many applications.

In flammability tests, PIR and PUR foams containing Terate polyols result in excellent char formation with minimal shrinkage and high weight retention.* In many formulations, the unique aromatic backbone of Terate polyols reduces or eliminates the need for expensive flame retardants.

* As demonstrated in ASTM E-84 and Factory Mutual calorimeter testing with HCFC 141b, pentane, and partially water-blown foams.

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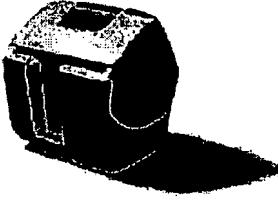
A Leader in the Industry

New product development, experienced technical service and computerized process control make KoSa's Terate polyols an industry leader. Market demands, such as blowing agent replacement and increased polyester polyol ratios, create challenges for foam formulators. KoSa's Terate professionals work proactively with customers and co-suppliers to develop optimal Terate-based PUR and PIR formulations.

As the world's largest producer of dimethyl terephthalate (DMT) - the raw material source for Terate Polyols - we can ensure that our customers receive an uninterrupted supply of consistent, high-quality products.

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Our Growth



Our Terate polyols were first produced in 1974 by Hercules at its Wilmington, NC, USA, site. Since 1989 when the current Terate team was formed, production has increased eight-fold and continues to increase at our newest production facility in Vlissingen, Netherlands.

Although our name has changed over the years - from Hercules to Cape Industries to Hoechst Celanese, and now to KoSa - our commitment to polyester and new applications for Terate polyols has remained constant. With continued enhancements of our products, KoSa provides the best polyester polyols for many applications in the urethane industry.

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Product Advantages

KoSa Terate polyols are ultimately designed to give our customers greater flexibility and control with their products. Additionally, our experience and capabilities provide customers with:

- Industry-leading technical service in formulation and production
- Reliable supply of internal raw material available
- Computerized quality process control
- Excellent flame-resistance results
- Multi-property product line
- Consistent quality products
- Blowing agent compatibility
- Cost advantage over polyethers
- High aromatic content
- Good flow properties
- Uniform reactivity

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Standard Product Information



Terate polyols are available in the following basic series featuring a variety of options in color, viscosity, acidity, processability, hydroxyl value and functionality. This list includes typical property ranges for each series. Please refer to data sheets available from your KoSa representative for actual product specifications and applications.

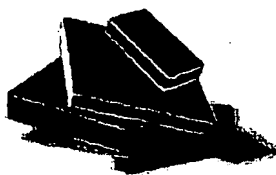
Value Range						
Product Series	Hydroxyl Value (mgKOH/g)	Viscosity (cps@25°C)	Functionality	Acidity (mgKOH/g)	Average Equivalent Weight	Specific Gravity (g/ml)
Terate 2000	280 - 335	3,000 - 22,000	2.3	0.5 - 4.0	181	1.2
The original Terate polyol with high functionality use in bunstock, panel, pour-in-place, spray and foundry systems. Available in lower acid numbers.						
Terate 2500	225 - 275	2,700 - 7,700	2.0	0.4 - 2.0	238	1.2
A polyol series with excellent flammability in polyisocyanurate foams with minimal shrinkage and high weight retention. In many formulations, the unique aromatic backbone reduces or eliminates expensive flame retardants. Used in laminate, panel, pour-in-place and spray systems.						
Terate 3000*	230 - 255	2750 - 7,500	2.0	0.6 - 1.2	230	1.2
A series of polyols developed for hydrocarbon blown foam applications with improved characteristics over the 2500 series.						
Terate 4000*	295 - 350	1,500 - 6,000	2.0 - 2.2	0.2 - 1.5	175	1.2
An amber polyol series used in appliance systems and for other low viscosity requirements. Similar to our 2000 series, but with reduced viscosity.						
Phenrez®*	50 - 100	700 - 10,000	-	2.0 - 10	-	1.13
A dark, high-polar, liquid aromatic polyester resin used in foundries producing furan no-bake (FNB) resin systems.						

SEE MATERIAL SAFETY DATA SHEET FOR SAFETY INFORMATION. Because we cannot anticipate or control the many different conditions under which this information and our products may be used, we do not guarantee the applicability or the accuracy of this information or the suitability of our products in any given situation. Users of our products should conduct their own tests to determine the suitability of each such product for their particular purposes. The products discussed are sold without warranty, either expressed or implied, and the buyer assumes all responsibility for loss or damage arising from the handling and use of our products. Additionally, statements concerning the possible use of our products are not intended as recommendations to use our products in the infringement of any patent.

*Please check with a KoSa representative about availability in your area.

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Guidelines for Storage and Handling



Terate polyols can be stored and handled in tanks made of carbon steel, stainless steel, fiberglass or other conventional construction materials. Storage temperatures should be kept below 60°C (140°F) to maintain product integrity. Storage vessels and process tanks also should be protected with dry air [minimum 4.4°C (-40°F bulb)] or nitrogen to prevent uptake of atmospheric moisture. Please see the MSDS for specific details on handling individual products.

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Availability and Reliability

Terate polyols are shipped worldwide in lined, closed-head drums, tank trucks, and tank cars from KoSa's US and European facilities. Samples are available upon request. Our Terate polyol team will be glad to arrange a delivery system to best meet your needs.

Terate® and Phenrez® are registered trademarks of KoSa.

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Customer Service, Sales, and Technical Information

Inside the United States, dial toll-free 1-800-562-0172

Outside the United States, dial:

North America, South America and Asia

Customer Service 1-910-341-5947

Fax 1-910-341-5951

Europe, Africa and Middle East

Customer Service 49(0)-69-305-14789

Fax 49(0)-69-305-16315

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About Polyols

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Polyurethanes are based the exothermic reaction of polyisocyanates and polyol molecules. Many different kinds of polyurethane materials are produced from a few types of isocyanates and a range of polyols with different functionality and molecular weights. Some of the diversity of functionality depends on whether the polyols are based on polyether or polyesters. Condensation based polyols are used primarily in the construction and building industries for efficient insulation in roofs, wall cavities, and flooring. Polyether polyols are used in a wide range of rigid and flexible polyurethane applications, including energy saving refrigeration insulation, industrial sealants, cushion foam, and construction and building materials.

Polyether polyols contain the repeating ether linkage $-R-O-R-$ and have two or more hydroxyl groups as terminal functional groups. They are manufactured commercially by the catalyzed addition of epoxies (cyclic ethers) to an initiator. The most important of the cyclic ethers by far are propylene oxide and ethylene oxide, with smaller quantities of butylenes oxide also being consumed. These oxides react with active hydrogen-containing compounds (called initiators), such as water, glycols, polyols and amines; thus, a wide variety of compositions of varying structures, chain lengths and molecular weights is theoretically possible. By selecting the proper oxide (or oxides), initiator, and reaction conditions and catalysts, it is possible to synthesize a series of polyether polyols that range from low-molecular-weight polyglycols to high-molecular-weight resins. Most polyether polyols are produced for polyurethane applications; however, other end uses range from synthetic lubricants and functional fluids to surface-active agents.

Since these polymers contain repeating alkylene oxide units, they are often referred to as polyalkylene glycols or polyglycols. The terms *polyglycol* and *polyether polyol* are used interchangeably; however, the term *polyalkylene glycol* is used when these types of products are used in nonpolyurethane applications. The physical properties of the polyols are influenced primarily by the functionality of the initiator molecules and by the type and quantity of alkylene oxide and hydroxyl groups present in the polyol. In general, the functionality of the polyether is carried over from the functionality of the initiator used.

Two types of urethane polyols are prepared from propylene oxide. The first type results from the reaction of propylene oxide with compounds having an active hydrogen (usually donated by a hydroxyl or amine group); these polymers are typically atactic. Polymers of the second type are essentially those of propylene oxide itself and are commonly called polypropylene oxide or polypropylene glycol; they are in most cases isotactic. Mixtures of atactic and isotactic polymers may also occur.

The following table lists most of the major commercially available polyether polyol types used in urethane manufacture, plus the initiators and cyclic ethers (oxides) used in their preparation:

Selected Commercial Polyether Polyols and Reactants

Product	Initiator	Cyclic Ether
Difunctional <ul style="list-style-type: none"> ➤ Polypropylene Glycol (PPG) ➤ Polyethylene Glycol (PEG) ➤ Polyoxypropylene-Polyoxy-ethylene Block Copolymer ➤ Polytetramethylene Ether Glycol (PTMEG) ➤ Aromatic Diol ➤ Amine Adducts 	<ul style="list-style-type: none"> ➤ Water or propylene glycol ➤ Water or ethylene glycol ➤ Water, propylene glycol or glycerin * ➤ Water ➤ Bisphenol A ➤ Primary monoamines ** 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Ethylene oxide ➤ Propylene oxide and ethylene oxide ➤ Tetrahydrofuran ➤ Propylene oxide or ethylene oxide ➤ Propylene oxide or ethylene oxide
Trifunctional <ul style="list-style-type: none"> ➤ Glycerin Adduct ➤ Trimethylolpropane Adduct ➤ Trimethylolethane Adduct 	<ul style="list-style-type: none"> ➤ Glycerin ➤ Trimethylolpropane ➤ Trimethylolethane 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide
Tetrafunctional <ul style="list-style-type: none"> ➤ Pentaerythritol Adduct ➤ Ethylenediamine Adduct ➤ Phenolic Resin Adduct ➤ Methyl Glucoside Adduct 	<ul style="list-style-type: none"> ➤ Pentaerythritol ➤ Ethylenediamine ➤ Phenolic resin ➤ Methyl Glucoside 	<ul style="list-style-type: none"> ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide ➤ Propylene oxide
Pentafunctional <ul style="list-style-type: none"> ➤ Diethylenetriamine Adduct 	<ul style="list-style-type: none"> ➤ Diethylenetriamine 	<ul style="list-style-type: none"> ➤ Propylene oxide
Hexafunctional <ul style="list-style-type: none"> ➤ Sorbitol Adducts 	<ul style="list-style-type: none"> ➤ Sorbitol 	<ul style="list-style-type: none"> ➤ Propylene oxide or ethylene oxide
Octafunctional <ul style="list-style-type: none"> ➤ Sucrose Adducts 	<ul style="list-style-type: none"> ➤ Sucrose 	<ul style="list-style-type: none"> ➤ Propylene oxide

* Other compounds, including trimethylolpropane, trimethylolethane, pentaerythritol, ethylenediamine, sorbitol and sucrose, can also be used as initiators for block copolymers based on propylene oxide and ethylene oxide.

** Primary monoamines include aniline, cyclohexylamine and others. The compositions made from these amines and oxides are principally surface-active agents.

During the late 1980s, the polyurethane industry was faced with a major change in manufacturing practice to reduce foam blowing using chlorofluorocarbons (CFCs). The once widely used CFC-11 (CCl_3F) and, to a lesser extent, CFC-12 (CCl_2F_2), have been replaced with other blowing agents such as hydrochlorofluorocarbons (HCFCs) or other nonfluorocarbon-based blowing agents that have lower ozone depletion potentials. For some time, scientific data have shown that these "hard" fluorocarbons (they do not decompose) are the cause of an increasing depletion of the ozone layer above the earth's atmosphere.

The industry is working with two HCFCs: Cl_2FCH_3 , called HCFC-141b, and CHCl_2CF_3 , called HCFC-123. These materials decompose, permitting the production of polyurethane foams with acceptable performance characteristics, but they are more expensive than the hard fluorocarbons they are designed to replace. Commercial quantities of some of the new HCFCs have been available since 1992.

The industry has responded with the development of new manufacturing methods, machinery and auxiliary blowing agents to replace conventional fluorocarbon blowing agents. Flexible foam is produced using a water-blown technology—where the foam is blown by carbon dioxide gas generated when

water in the formulation reacts with toluene diisocyanate. Methylene chloride, acetone or hydrocarbons are sometimes used to replace some of the fluorocarbon. Rigid foams now use formulations with HCFCs replacing CFC-11.

MANUFACTURING PROCESSES

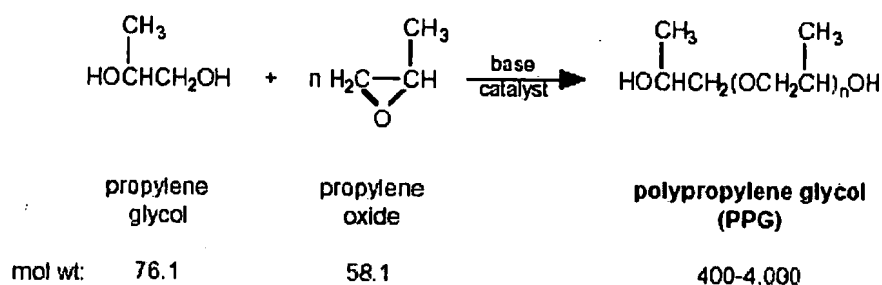
POLYOLS BASED ON PROPYLENE OXIDE

Polyether polyols based on propylene oxide (PO) are produced by the base-catalyzed reaction of propylene oxide with an initiator compound having active hydrogens (e.g., hydroxyl or amine groups). When small quantities of ethylene or other alkylene oxides are also present, block copolymers are produced.

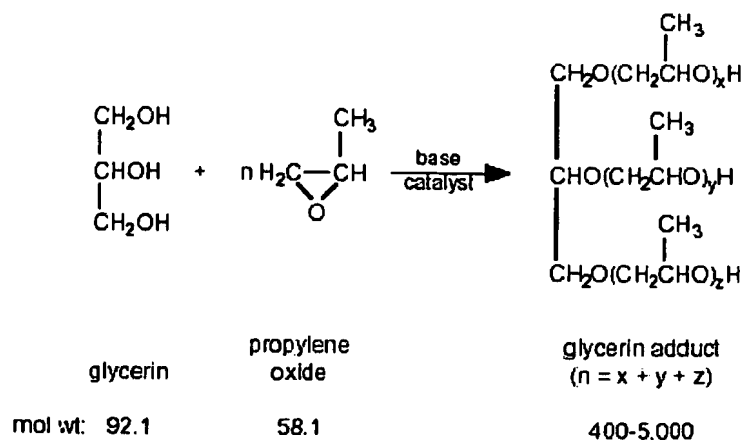
Potassium hydroxide is the basic catalyst most often employed. The initiator used depends on the type of polyurethane (i.e., flexible, rigid or nonfoam) to be produced from the polyhydric alcohol. This reaction is carried out by a discontinuous batch process at elevated temperatures and pressures and under an inert atmosphere (i.e., under a nitrogen blanket). After the desired degree of polymerization has been achieved, the catalyst is neutralized and removed by filtration. The polyol is subsequently purified and additives such as antioxidants are added.

Simplified reaction equations for the major polyurethane polyether polyols are illustrated below.

POLYPROPYLENE GLYCOL (PPG)



POLYOL ADDUCTS

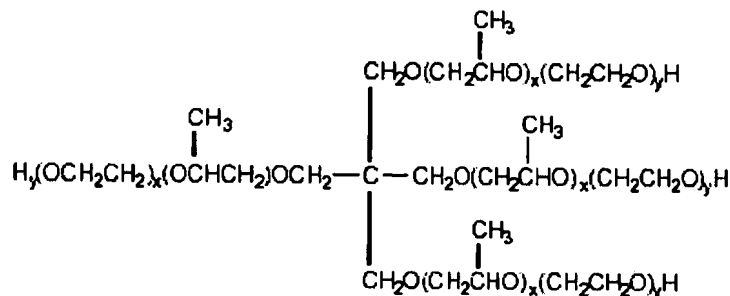


The manufacture of other polyol adducts (pentaerythritol, trimethylolpropane, trimethylolethane, sucrose and sorbitol) is similar to the above process. The manufacture of corresponding amine adducts generally follows the same process.

BLOCK COPOLYMERS

Block copolymers are commercially available that are initiated with glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, sucrose and several other compounds. They are based almost entirely on propylene oxide; however, the secondary hydroxyl groups are capped with ethylene oxide to yield terminal primary hydroxyl groups. Since primary hydroxyl groups are more reactive than secondary hydroxyl groups, these polyols are more reactive with isocyanates.

Block copolymers can be represented by the general formula shown below, where the initiator is a polyhydric alcohol (pentaerythritol initiator is shown below).



Small quantities of mixed and alternating block copolymers are also produced. In these block copolymers the ethylene oxide is incorporated into the alkylene oxide chains. These products may also be end-capped with ethylene oxide.

Tetrafunctional block copolymers initiated with ethylenediamine are also commercially available. The amine is reacted with propylene oxide to yield the totally hydroxypropylated ethylenediamine, which is further reacted with propylene oxide and then with ethylene oxide to form the desired polyether polyol.

MODIFIED POLYOLS BASED ON PROPYLENE OXIDE

Polymer Polyols

Polymer polyols are also referred to as graft polymer polyols, graft polyols, or copolymer polyols; all of these terms are used to describe products that are basically stable dispersions of vinyl polymers in polyols. Polymer polyols are produced by the in-situ polymerization of a vinyl monomer in a base polyol.

The base polyol is typically a glycerin-initiated triol that has been end-capped with ethylene oxide (approximately 80-85% primary hydroxyl groups). Styrene and acrylonitrile are the vinyl monomers most often used. The styrene-acrylonitrile copolymers are chosen because in the preparation of graft polyols, acrylonitrile—due to its grafting tendency—provides a very important linkage between the vinyl polymer chain and the polyol chain. In addition to the graft copolymerates, the polymer polyol contains the homopolymers of styrene and acrylonitrile dispersed in unaltered polyether polyols. The styreneacrylonitrile solids content of the polyol ranges from 5% to 45%. The solids content of the polyol depends on the end-use market; those having a high solids content are used

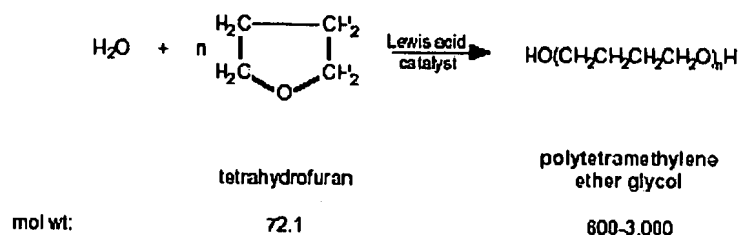
in carpet underlay while those having a lower solids content are used principally for molding applications such as automobile seating and furniture. Polymer polyols may be used alone but are typically used in blends with other highly reactive polyols in the production of high-resilience (HR) flexible foams. The principal benefits derived from the use of these materials are improved processing—due largely to a "cell opening" effect in HR applications—and enhancement of modulation, which in foams is measured as load bearing. Polymer polyols alone or in blends with conventional polyols permit the production of a range of foams with medium to high load-bearing properties. BASF, Dow, Lyondell Chemical and Olin are the primary producers of polymer polyols in the United States.

Polyurea Polyols

Another technically important group of modified polyols based on propylene oxide are the polyurea polyols, also known as PHD polyethers. Polyurea polyols are produced by the in-situ polyaddition reaction of isocyanates with amines in a base polyol. The isocyanate reacts more quickly with amines than polyols. Consequently, the isocyanate preferentially reacts with the amine (e.g., hydrazine) to form a urea group; the polyol functions only as a dispersion medium. The concentration of solids is limited by the viscosity of the product. However, polyurea solids content of 20-40% can usually be achieved. Polyurea polyols are used in blends with other highly reactive polyols in the production of HR foams and for reaction injection-molded (RIM) applications. Bayer is a producer of polyurea polyols in the United States.

POLYOLS BASED ON TETRAHYDROFURAN

Polytetramethylene ether glycol (PTMEG) of 650-2,000 molecular weight is prepared by the Lewis acid catalyzed polymerization of tetrahydrofuran.



PTMEG is, depending on its molecular weight, a liquid or a white waxy solid that melts to a clear liquid at 38°C (100°F). BASF Corporation, DuPont and QO Chemicals are the producers of PTMEG in the United States. The product is used in polyurethane elastomers and spandex fibers.

ENVIRONMENTAL ISSUES

Polyether polyols do not present an industrial hygiene problem, when used according to the relevant regulations. However, environmental issues are increasingly important in the polyurethane and polyurethane raw materials businesses. The industry has had to find replacements for HCFC blowing agents. It is now addressing the recyclability and reclaimability of used products. Some of the developing processes produce recovered polyols from polyurethane wastes.

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